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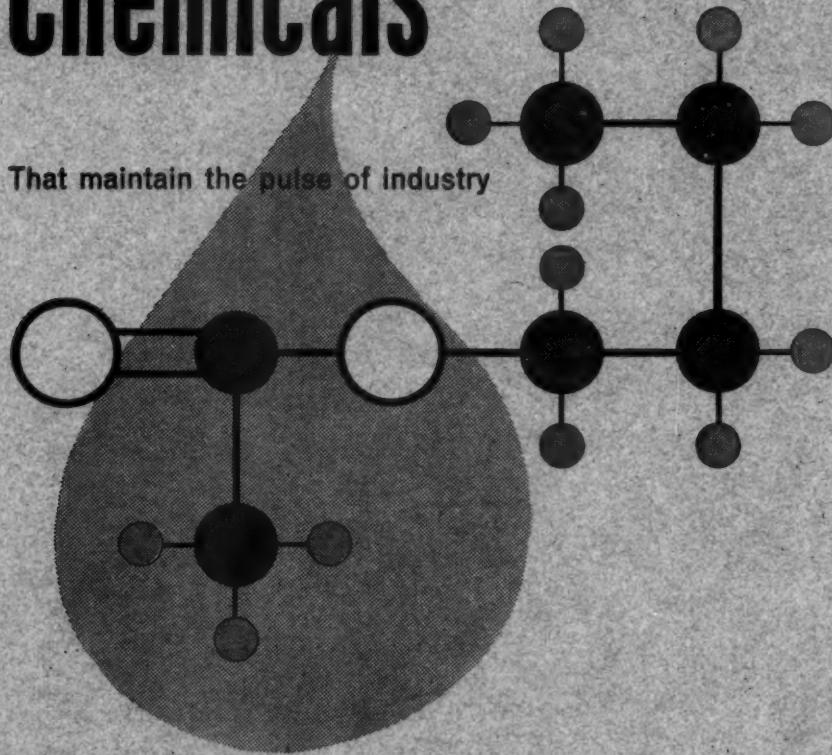
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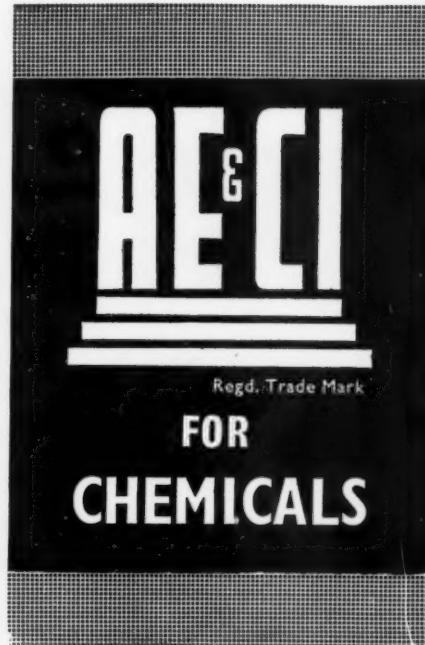
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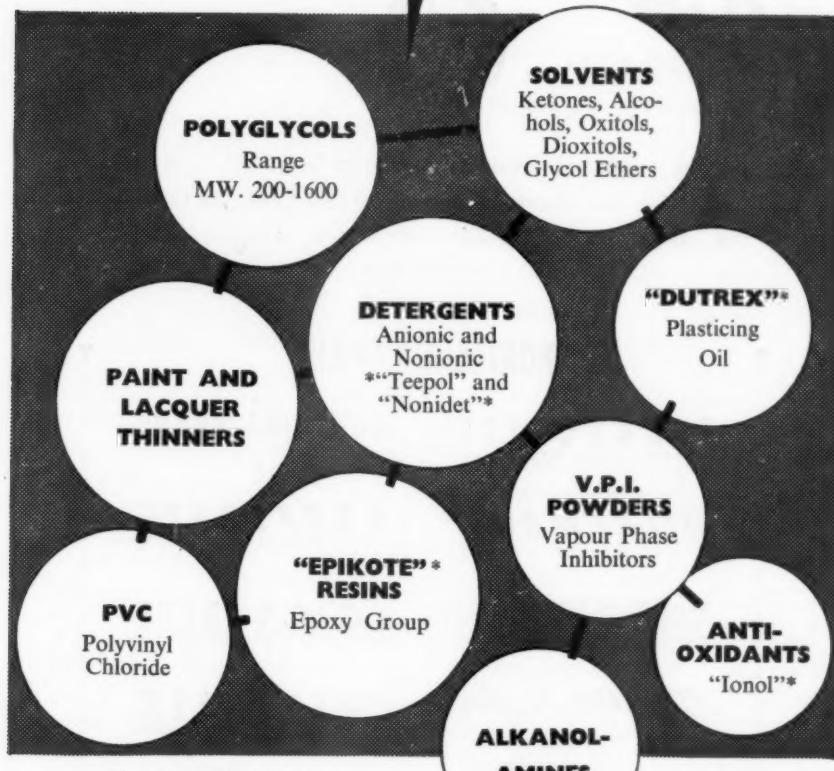
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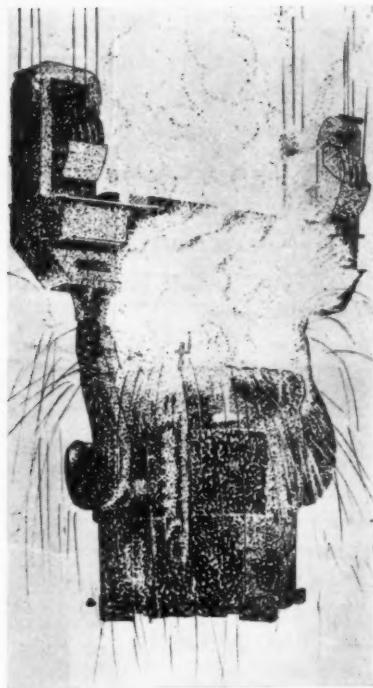
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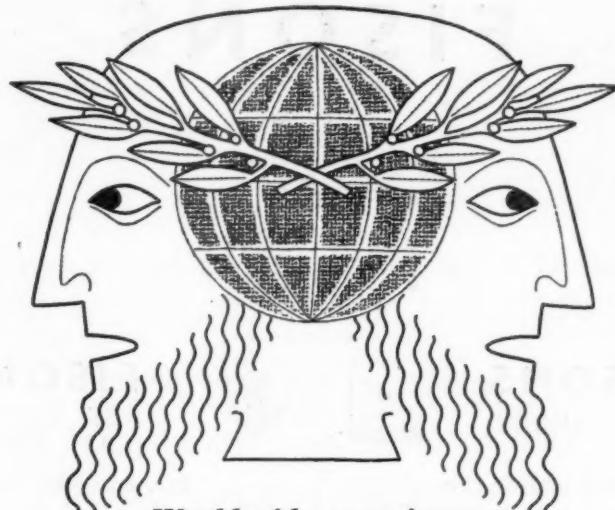
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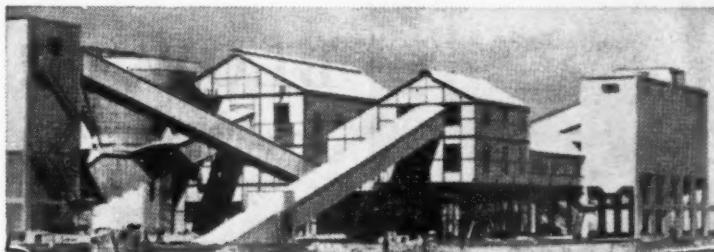
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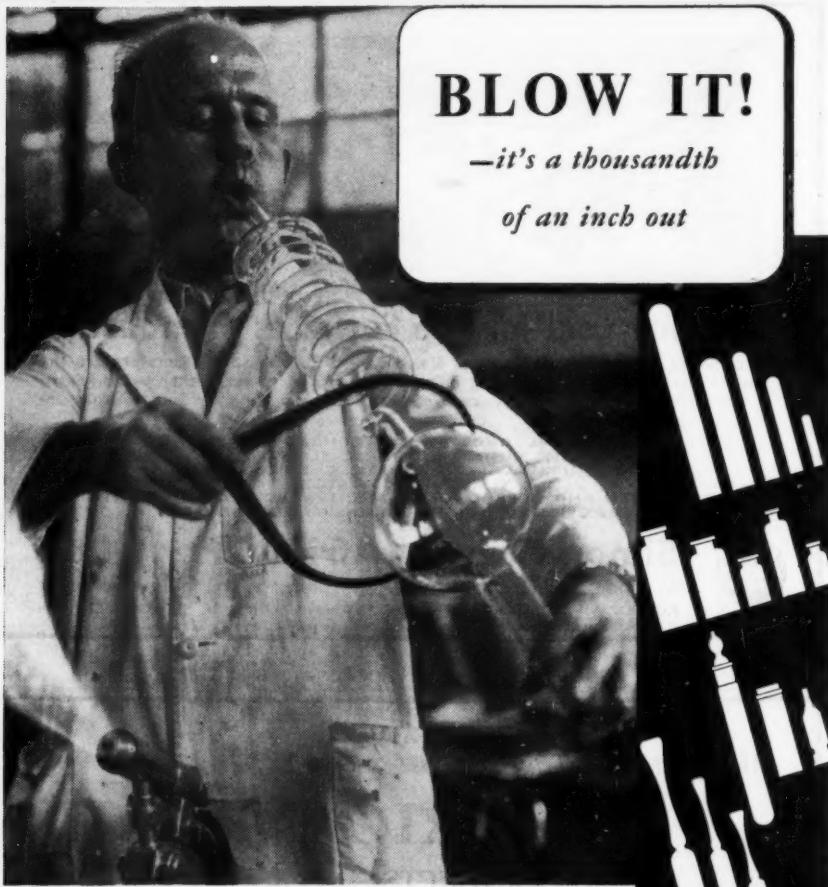


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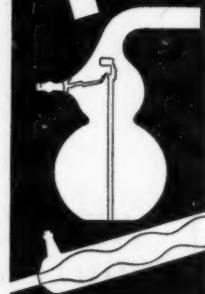
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## X-RAY CRYSTALLOGRAPHY OF BIURET AND RELATED COMPOUNDS

by

G. F. G. KNIPE and J. W. MENARY

### OPSOMMING

X-straal diffraksie-gegewens vir poeivormige materiaal en enkel kristalle word aangegee vir die verbindings biuret, biuretmonohidraat en biurea. Die kompleks urea-biuret verbinding waaroor voorheen verslag gedoen is, is 'n polimorfie modifikasie van biuret.

### SUMMARY

X-ray powder diffraction patterns and single crystal data are presented for the compounds biuret, biuret monohydrate and biurea. The complex urea-biuret compound previously reported is a polymorphic modification of biuret.

### INTRODUCTION

During studies on fertilizer grade urea, X-ray data were obtained for biuret, biuret monohydrate and biurea. Our results have shown that the powder pattern for biuret in the A.S.T.M. X-ray Powder Data File represents a mixture of biuret and biuret monohydrate, and is therefore misleading. Attempts to synthesise the complex urea-biuret compound reported by Rollet and Cohen-Adad<sup>1</sup> resulted only in the formation of a new polymorphic modification of biuret.

### EXPERIMENTAL

Biuret was recrystallized from absolute alcohol, biuret monohydrate from N sodium hydroxide solution and biurea from water. Chemical analysis of the hydrated biuret showed that the water content was 79% of that calculated for the monohydrate. X-ray powder diffraction patterns were obtained with a Berthold recording diffractometer. Single crystal data were obtained with a Unicam 57.3 mm diameter Weissenberg camera.

In an attempt to synthesise the 2:1 urea-biuret complex, approximately equal weights of urea and biuret were melted together. X-ray diffraction analysis of the cooled mixture showed the presence of urea and a previously unreported compound. Urea was removed from the mixture by treatment with hot acetone. When the resulting solid was recrystallized from water, biuret monohydrate was the only product isolated.

### RESULTS

The X-ray powder diffraction patterns for the two modifications of biuret, for biuret monohydrate, and for biurea are reported in Tables I to IV.

### SINGLE CRYSTAL STUDIES

#### *Biuret*

The room temperature modification of biuret is monoclinic. Lattice parameters calculated from single crystal measurements are:  $a=15.34\text{\AA}$ ,  $b=6.60\text{\AA}$ ,  $c=9.26\text{\AA}$ ,  $\beta=92^\circ$ . These results were used to assign indices to the powder reflections in Table I.

Lattice parameters determined from the powder data are:  $a=15.43\text{\AA}$ ,  $b=6.587\text{\AA}$ ,  $c=9.294\text{\AA}$ ,  $\beta=91^\circ 38'$ . Hargreaves and Taylor<sup>2</sup> report values:  $a=9.20\text{\AA}$ ,  $b=6.6\text{\AA}$ ,  $c=15.4\text{\AA}$ ,  $\beta \approx 90^\circ$ . Using the more accurate parameters derived from our powder data, the density calculated for 8 molecules biuret per unit cell is  $1.450 \text{ g cm}^{-3}$ , in agreement with published<sup>2,3</sup> values of  $1.452$  and  $1.467 \text{ g cm}^{-3}$ .

Extinctions observed showed that the space group is either  $Cc$  or  $C2/c$ . A test<sup>4</sup> for pyroelectric properties gave positive results. Hettish and Schleede<sup>5</sup> have also shown that biuret is piezoelectric. These properties are characteristic of non-centro-symmetric crystal classes. Consequently the space group of biuret is  $Cc$ .

#### *Biuret monohydrate*

Biuret monohydrate is monoclinic. Lattice parameters derived from single crystal measurements are:  $a=7.89\text{\AA}$ ,  $b=17.70\text{\AA}$ ,  $c=3.66\text{\AA}$ ,  $\beta=95^\circ$ . More accurate values derived from powder diffraction data are:  $a=7.956\text{\AA}$ ,  $b=17.78\text{\AA}$ ,  $c=3.651\text{\AA}$ ,  $\beta=95^\circ 13'$ . For four molecules biuret 0.79-hydrate per unit cell the density calculated from the powder X-ray data is  $1.516 \text{ g cm}^{-3}$ . A value of  $1.516 \text{ g cm}^{-3}$  was found by flotation.

Extinctions observed established that the space group was  $P2_1/n$ .

#### *Biurea*

Biurea is triclinic. Unit cell parameters derived from moving film photographs are:  $a=4.74\text{\AA}$ ,  $b=7.22\text{\AA}$ ,  $c=10.7\text{\AA}$ ,  $\alpha=108^\circ 54'$ ,  $\beta=119^\circ 02'$ ,  $\gamma=107^\circ 38'$ . For two molecules biurea per unit cell the calculated density is  $1.557 \text{ g cm}^{-3}$ . The approximate value found by flotation was  $1.58 \text{ g cm}^{-3}$ .

A test<sup>4</sup> for pyroelectric properties was negative, indicating that the space group is  $P\bar{1}$ . However, the alternative space group,  $P1$ , is not eliminated since a very feeble pyroelectric effect would not have been detected.

TABLE I  
*Powder diffraction data for the room temperature modification of biuret*

d (Å)	I	hkl
7.75	100	200
6.06	1	110, 20 <sup>7</sup>
5.98	15	111, 111
4.68	30	002
4.04	56	310, 20 <sup>2</sup>
3.93	6	202
3.86	16	400
3.75	50	311
3.72	10	112
3.089	55	312, 003
3.027	10	312
2.888	4	22 <sup>7</sup>
2.791	12	113, 510
2.696	2	511
2.659	4	511
2.569	12	600
2.490	10	420, 313
2.416	5	427, 512
2.218	2	422, 602
2.189	3	114, 422
2.120	4	513, 701
1.971	5	
1.927	6	
1.656	9	
1.543	3	

TABLE II  
*Powder diffraction data for the high temperature modification of biuret*

d (Å)	I*	d (Å)	I*
6.83	10	2.71	10
5.79	30	2.58	50
5.42	10	2.53	10
5.34	10	2.41	50
4.84	80	2.39	50
4.66	30	2.34	30
4.60	50	2.29	100
4.24	50	2.16	10
4.01	50	2.120	10
3.82	50	2.082	10
3.65	50	2.054	10
3.61	50	2.039	10
3.40	90	2.002	30
3.30	30	1.910	30
3.21	70	1.863	30
3.09	10	1.824	30
2.99	30	1.798	10
2.93	10	1.688	10
2.89	10	1.606	30
2.84	50	1.569	10
2.74	10		

\* Approximate scale.

TABLE III  
Powder diffraction data for bireta monohydrate

d (Å)	I	hkl	d (Å)	I	hkl
8.96	25	020	5.71	70	010
7.30	30	110	4.29	2	105
4.77	25	130	4.15	12	170
3.97	4	200	3.86	16	002
3.86	20	210	3.47	100	100
3.61	2	220	3.37	5	027
3.56	25	011	3.25	14	120
3.36	30	111, 021	3.070	8	151
3.30	8	230	2.942	50	117
3.21	100	101, 121	2.846	32	021
3.151	20	111	2.592	8	101
3.011	15	121	2.448	4	122
2.962	10	131, 060	2.416	13	110, 172
2.815	5	131, 041	2.365	6	512
2.778	5	211, 160	2.311	3	122
2.712	6	141	2.287	14	
2.538	80	211, 320, 237, 051	2.250	4	
2.465	5	221, 151	2.191	2	
2.410	20	330, 170	2.147	3	
2.298	3	061	2.074	4	
2.221	15	311, 241, 080	2.046	10	
2.206	10	251	1.991	2	
2.173	3	321, 161	1.957	2	
2.141	8	270, 180	1.904	6	
2.090	3	331	1.846	4	
1.970	2	410, 360	1.789	2	
1.778	6	351, 0, 10, 0	1.767	2	
1.678	6		1.725	14	
1.593	7		1.683	8	
			1.623	4	
			1.541	6	

TABLE IV  
Powder diffraction data for bireta

d (Å)	I	hkl	d (Å)	I	hkl
5.71	70	010	5.71	70	010
4.29	2	105	4.29	2	105
4.15	12	170	4.15	12	170
3.86	16	002	3.86	16	002
3.47	100	100	3.47	100	100
3.37	5	027	3.37	5	027
3.25	14	120	3.25	14	120
3.070	8		3.070	8	
2.942	50		2.942	50	
2.846	32		2.846	32	
2.592	8		2.592	8	
2.448	4		2.448	4	
2.416	13		2.416	13	
2.365	6		2.365	6	
2.311	3		2.311	3	
2.287	14		2.287	14	
2.250	4		2.250	4	
2.191	2		2.191	2	
2.147	3		2.147	3	
2.074	4		2.074	4	
2.046	10		2.046	10	
1.991	2		1.991	2	
1.957	2		1.957	2	
1.904	6		1.904	6	
1.846	4		1.846	4	
1.789	2		1.789	2	
1.767	2		1.767	2	
1.725	14		1.725	14	
1.683	8		1.683	8	
1.623	4		1.623	4	
1.541	6		1.541	6	

## DISCUSSION

X-ray analysis has shown that little or no reaction takes place between urea and biuret when these compounds are melted together. The new solid phase obtained can only have been a polymorphic modification of biuret, stabilized by the presence of urea. Such effects are common for organic compounds.<sup>6</sup> This explanation would satisfactorily account for the results of Rollet and Cohen-Adad<sup>1</sup> for the urea-biuret system.

Further work is in progress to establish the range of stability of the high temperature modification of biuret, and to determine the crystallographic constants.

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## REFERENCES

- <sup>1</sup> Rollet and Cohen-Adad, *Compt. rend.*, 1949, **229**, 199.
- <sup>2</sup> Hargreaves and Taylor, see Haworth and Mann, *J. Chem. Soc.*, 1943, 603.
- <sup>3</sup> Beck, *Wien. Chem. Ztg.*, 1943, **46**, 18.
- <sup>4</sup> Robertson, *J. Chem. Soc.*, 1935, 615.
- <sup>5</sup> Hettish and Schleede, *Z. Physik.*, 1928, **50**, 249.
- <sup>6</sup> Mitchell and Ryland, *Mikrochim. Acta*, 1956, 422.

## APPLICATION OF E.D.T.A. TO THE DETERMINATION OF ZINC- ACCURACY AND PRECISION OF ANALYSIS

by

J. LACY

### OPSOMMING

Die titrasie van sink met E.D.T.A. kan geslaagd toegespas word vir die bepaling van sink in 'n verskeidenheid stowwe. Die akkuraatheid en noukeurigheid van die analise word aangedui en 'n vergelyking met die ferrosianiet metode word gemaak. Met behulp van die metode kan 'n bepaling in vyf-en-twintig minute gedoen word.

### SUMMARY

The titration of zinc with E.D.T.A. has been applied successfully to the determination of zinc in a number of different materials. The accuracy and precision of analyses are recorded and a comparison is made with the ferrocyanide method. The method is rapid and enables a determination to be completed in about 25 minutes.

### INTRODUCTION

A rapid and accurate method was required to replace the ferrocyanide procedure for the determination of zinc in zinc ash, zinc ammonium chloride solution, zinc chloride and zinc sulphate. Of these materials, the most impure one is zinc ash which contains about 70% zinc and up to 2% iron, 1% aluminium, 10% lead and 3% copper, together with smaller amounts of silicon, magnesium, tin, calcium and silver. The ferrocyanide method involves the titration of zinc with standard potassium ferrocyanide solution after removal of interfering elements by precipitation of their sulphides and hydroxides. Diphenylbenzidine was used as the indicator. In this estimation it is essential to work under uniform conditions to obtain concordant results.<sup>1</sup> Other indicators<sup>2</sup> such as naphthidine are stated to be superior to diphenylbenzidine for the titration of zinc with ferrocyanide solution. The difficulty, however, lies not with the actual titration but with the removal of interferences prior to titration. The removal of interfering elements by means of hydrogen sulphide is tedious and can lead to inaccuracies.

Kinnunen and Merikanto<sup>3</sup> have applied Schwarzenbach's general E.D.T.A. method<sup>4,5</sup> to the determination of zinc in brass. Relatively few figures are quoted, however, and there is no indication of the precision of the analysis. It was considered that the best method would be one involving the general procedure of Schwarzenbach in which zinc is titrated with E.D.T.A. using Eriochrome Black T as indicator. Most of the interfering elements in materials such as zinc ash can be eliminated by complex formation and precipitation.

### EXPERIMENTAL

#### *Determination of zinc in synthetic solutions*

Iron, aluminium and lead were removed by precipitation as their hydroxides. Interference due to copper was eliminated by the formation of its cyanide complex with potassium cyanide solution. Zinc is also complexed with potassium cyanide but is released from its complex by the addition of formaldehyde, whereas the copper cyanide complex, being more stable, is not attacked. The liberated zinc was then

titrated with E.D.T.A. using Eriochrome Black T as the indicator. Although interference by calcium and magnesium is not eliminated by this procedure, the amounts usually present in materials such as zinc ash are so small that they are unlikely to affect the results. This is confirmed by the results in Table I, where the quantities of calcium and magnesium are greater than would be encountered in actual samples.

The E.D.T.A. procedure and the old method (ferrocyanide) were tested on solutions resembling those which would be obtained from zinc ash, zinc ammonium chloride and zinc sulphate, but containing accurately known amounts of pure zinc with different amounts of impurities. The same pure zinc solution was used for the standardisation of the E.D.T.A. The synthetic solutions of zinc ammonium chloride and zinc sulphate contained 30%  $ZnCl_2$ , 25%  $NH_4Cl$ , 3% Fe, 1% Al, 3% Cu and 26%  $ZnSO_4$ , 3% Fe, 1% Al, 2.5% Cu respectively. The results obtained are shown in Table I.

TABLE I  
*Testing of the E.D.T.A. method on synthetic solutions*

Solution tested	E.D.T.A. Method			Ferrocyanide Method			Amounts of impurities added
	Mean % Zn recovered	No. of detns.	Std. Dev.	Mean % Zn recovered	No. of detns.	Std. dev.	
*Synthetic zinc ash.	100.02	11	0.07	99.42	5	0.42	10mg Pb, 30mg Cu, 6mg Fe, 2mg Al
	99.90	4	0.06	—	—	—	20mg Pb, 30mg Cu, 6mg Fe, 2mg Al.
	100.32	12	0.14	—	—	—	30mg Pb, 30mg Cu, 6mg Fe, 2mg Al.
	100.20	11	0.13	—	—	—	30mg Pb, 30mg Cu, 6mg Fe, 4mg Al.
	99.94	6	0.13	—	—	—	10mg Pb, 6mg Fe, 2mg Al, 0.2mg Si, Mg, Sn, 0.02mg Ca, Ag.
*Synthetic zinc ammonium chloride.	99.83	6	0.08	98.29	6	0.30	30mg Fe, 10mg Al, 30mg Cu.
*Synthetic zinc sulphate.	99.80	6	0.08	—	—	—	36mg Fe, 12 mg Al, 30mg Cu.

\*The amount of zinc per determination ranged from 0.13-0.16g.

It is evident, therefore, that the E.D.T.A. procedure is more accurate and precise than the ferrocyanide method, which gives low results and poor precision.

#### *Precision of analysis of actual samples*

The results obtained on a number of zinc samples are shown in Table II.

It will be observed from these results that the ferrocyanide method always gives lower results than the E.D.T.A. method. This is in accordance with the results given in Table I where the recovery of zinc was lower for the ferrocyanide method than for the E.D.T.A. method. Table II also shows that the E.D.T.A. procedure is usually more precise than the ferrocyanide method.

TABLE II  
*Precision of the two methods on actual samples*

Sample	E.D.T.A. method			Ferrocyanide method		
	Mean %	No. of dtns.	Std. dev.	Mean %	No. of dtns.	Std. dev.
Zinc ash (as Zn)						
No. 1	77.90	6	0.11	77.41	6	0.16
No. 2	71.93	18	0.08	—	—	—
Zinc ammonium chloride solution (as $ZnCl_2$ )						
No. 1	34.84	6	0.02	34.78	5	0.07
No. 2	30.32	12	0.04	—	—	—
Zinc sulphate solution (as $ZnSO_4$ )						
No 1	30.52	6	0.04	30.40	6	0.03
No. 2	26.30	12	0.03	—	—	—
Zinc chloride solution (as $ZnCl_2$ )						
No 1	67.76	6	0.05	67.55	6	0.22
No. 2	57.85	12	0.06	—	—	—
Zinc oxysulphate (as Zn)	43.13	6	0.08	—	—	—

*Recommended Procedure*

After dissolution of the sample and removal of insolubles, an aliquot portion containing about 0.15 g of zinc is transferred to a 500 ml Erlenmeyer flask. Concentrated nitric acid (5 ml) is added and the solution boiled to oxidise ferrous iron. The solution is then cooled slightly and concentrated ammonia added until a permanent precipitate is formed. Excess of ammonia solution (10 ml) is added, the solution cooled to about 60°C and 20% potassium cyanide solution (4 ml) added. The solution is filtered and the precipitate washed with 2% ammonia. When large amounts of lead are present it is sometimes necessary to refilter. The clear filtrate and washings are diluted to about 300 ml with water and 4% formaldehyde (25 ml) added, followed immediately by Eriochrome Black T solution (0.4 g per 100 ml absolute alcohol; 1-1.5 ml). The solution is titrated immediately and as rapidly as possible with 0.1M E.D.T.A. solution until the colour changes from wine red to blue. If large amounts of copper are present in the sample it is essential to complete the titration as quickly as possible after the addition of formaldehyde and indicator. If copper is absent from the sample the titration can be carried out more slowly.

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REFERENCES

- 1 Vogel, *A Text Book of Quantitative Inorganic Analysis*, 3rd Edition, Longmans, Green & Co., London, 1947, p. 463.
- 2 Belcher and Nutton, *J. Chem. Soc.*, 1951, 548.
- 3 Kinnunen and Merikanto, *Chemist Analyst*, 1952, **41**, 77.
- 4 Schwarzenbach and Schweiz, *Chem. Ztg.*, 1945, **28**, 377.
- 5 Schwarzenbach and Biederman, *Helv. Chim. Acta*, 1948, **31**, 331, 456, 459, 678.

## HEATS OF FORMATION OF HYDROXY-, FLUOR- AND CHLORAPATITES

by

A. J. GOTTSCHAL

### OPSOMMING

Die reaksiewarmte tussen hidroksie-, fluoro- en chloropatiete en salpetersuur van 20 en 30 persent sterkte is by 25°C bepaal met behulp van 'n kalorimeter van spesiale ontwerp. Deur gebruik te maak van die eksperimentele resultate en beskikbare gegewens in die literatuur is die vormingswarmte van die apatiete by 25°C bereken.

Die volgende waardes is verkry:

$$\begin{aligned}\Delta H_f &= -3231 \text{ kkal/mol vir hidroksieapatiet,} \\ \Delta H_f &= -3262 \text{ kkal/mol vir fluorapatiet} \\ \text{en } \Delta H_f &= -3172 \text{ kkal/mol vir chloropatiet.}\end{aligned}$$

### SUMMARY

The heats of reaction between hydroxy-, fluor- and chlorapatites and nitric acid of 20% and 30% strength were measured at 25°C using a calorimeter of special design. From the experimental results and available literature data, the heats of formation at 25°C of the apatites were calculated.

The following values were obtained:

$$\begin{aligned}\Delta H_f &= -3231 \text{ kcal/mole for hydroxyapatite,} \\ \Delta H_f &= -3262 \text{ kcal/mole for fluorapatite,} \\ \text{and } \Delta H_f &= -3172 \text{ kcal/mole for chlorapatite.}\end{aligned}$$

### INTRODUCTION

During the course of an extensive programme of research on the inorganic and physical chemistry of the reactions involved in the manufacture of superphosphate fertilizers and related products it became evident that knowledge of the heats of formation of those apatites, which form the major phosphate-containing constituents of natural rock phosphates, i.e. hydroxy-, fluor- and chlorapatites, is highly desirable.

The reactions selected for the indirect determination of these heats of formation values were those between the apatites and nitric acid. It was expected, and rightly so, that the reaction between an apatite and nitric acid is quite rapid and proceeds to a well-defined final state, thus enabling the direct calorimetric measurement of the heat of reaction.

### EXPERIMENTAL

The experiments were carried out in an isothermal air-jacketed calorimeter of special design, due consideration being given to the prevention of heat losses through the escape of gases and vaporised substances and to the requirement of quantitative mixing of the reactants. Constant temperature of the air-jacket, which completely enveloped the calorimeter unit, was ensured by passing a steady stream of air of constant temperature through the jacket.

### Apparatus

A Dewar vessel, 6 cm internal diameter and 18 cm high, constitutes the calorimeter unit (see Figs. I and II). The Dewar vessel is readily removed and replaced

so that it can be assembled before being lowered into position in the thermostat. The annular space between the Dewar vessel and the glass cylinder provides the air-jacket surrounding the calorimeter unit. The means of provision of a constant temperature air stream is readily appreciated from Fig. I. The air enters the bottom of the air-jacket through a jet set tangentially to promote its even distribution.

The Dewar vessel contains (see Fig. II) a reaction vessel with detachable vented condenser, a mechanically driven stirrer and a thermometer immersed in the calorimeter medium (350 g of distilled water). The vessel is closed with a thick cork, split longitudinally for easy assembly and provided with holes into which the various parts fit closely. The reaction vessel consists of a glass tube, approximately 2 cm in diameter, closed at one end and provided at the other end with a mercury seal and hand stirrer. One of the reactants is placed in the reaction vessel itself, while the other is placed in a thin-bottomed glass cup resting on the two indentations in the wall of the reaction vessel. The reaction is started by forcing the hand stirrer through the bottom of the glass cup. The stirrer is provided with a splash disc located just above the connection between the reaction vessel and the condenser when the stirrer is lowered fully. The condenser consists of a helically wound thin-walled glass tube, a receiver and a vent to the atmosphere. Its function is to prevent loss of heat from the calorimeter by the liberation of vapours and gases during the reaction.

#### *Chemicals*

Small amounts of hydroxy-, fluor- and chlorapatite were prepared synthetically. Hydroxyapatite was prepared according to the method of Hayek and Stadlmann<sup>1</sup>. With slight modification fluorapatite was prepared by the method of Egan *et al*<sup>2</sup> and chlorapatite by that of Torok<sup>3</sup> and Wallaeys<sup>4</sup>. X-ray and chemical analyses showed the prepared apatites to be of moderate to high purity, i.e. fluorapatite was approximately 97 per cent. and the hydroxy- and chlorapatites about 98.5 per cent. pure.

Ammonium nitrate and calcium hydroxide, both of analytical reagent quality (Merck A.G., *pro analysi*), were used for calibration purposes.

Nitric acid of the required concentration was prepared from concentrated acid of high purity (A.E. and C.I.—ARQ, 55% w/w) by dilution with distilled water.

#### *Observations*

Measurements were carried out at  $25^{\circ}\text{C} \pm 1^{\circ}\text{C}$ . The temperatures of the air-jacket and of the calorimeter unit were measured with Beckmann thermometers, set to cover the range without altering the amount of mercury in the reservoirs. Calibration of the Beckmann thermometers against a reference mercury-in-glass long stem thermometer (accuracy  $\pm 0.005^{\circ}\text{C}$ ) showed both Beckmann thermometers to record changes in temperature with the same accuracy if not better than the reference thermometer. The error in temperature differences, as read from the temperature-time graphs, was estimated at  $\pm 0.002^{\circ}\text{C}$ .

The temperature of the air-jacket was read at ten minute intervals; the temperature of the water inside the calorimeter unit was also read at ten minute intervals, during the initial and end periods of the experiment, but at one minute intervals during the reaction period. Time intervals were measured with a stop watch.

#### *Calibration of the calorimeter unit*

Calibration of the calorimeter involves the determination of the heat capacity of the completely assembled unit ( $W$ ), the overall heat transfer coefficient ( $F$ ) for heat transfer between the unit and the air-jacket, and the heat generating coefficient ( $f$ ) of the stirrer.

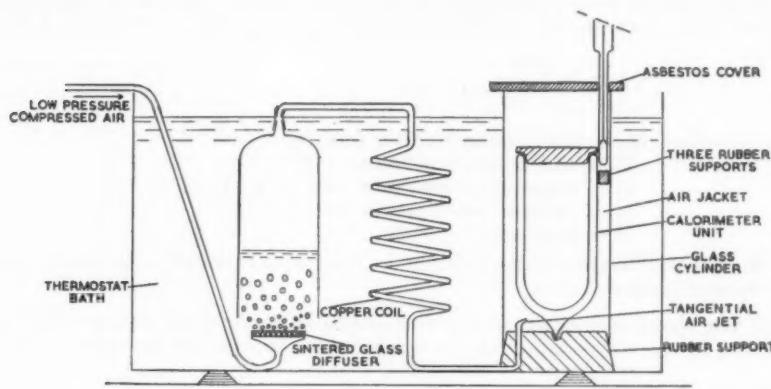


Fig. I—Experimental arrangement, showing flow of air to calorimeter air jacket and position of calorimeter unit

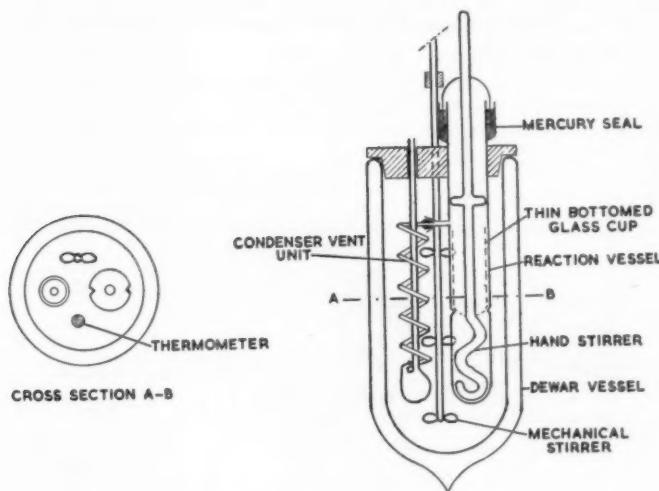


Fig. II—Calorimeter unit, showing detailed assembly

If the thermal head is small and if there is no transfer of heat by convection the flow of heat between the calorimeter and the air-jacket follows Newton's Law:

$$Q_F = F \cdot \int_{\theta_1}^{\theta_2} (t_c - t_j) \cdot d\theta \quad \dots \dots \dots \dots \dots \dots \dots \dots \dots \quad (1)$$

where,  $Q_F$  = total amount of heat transferred, cal

**F** = heat transfer coefficient, cal/°C min

$t_c$  = temperature inside the calorimeter unit, °C

$t_j$  = temperature of the air-jacket, °C

$\theta$  = time, min

In non-adiabatic calorimetry the value of the integral in equation (1) is usually found by graphical integration.

If the speed of rotation of the mechanical stirrer is kept constant the heat generated by the stirrer action can be taken to be a function of time only:

where,  $Q_f$  = total amount of heat generated by the stirrer, cal

$f$  = heat generating coefficient of the stirrer, cal/min

Employing a reaction of which the heat effect is known accurately three equations, each containing the three calibration constants, can be derived from the complete temperature/time curves. Fig. III is a typical example of a temperature/time plot obtained with the present apparatus. With reference to this graph the following three equations are derived.

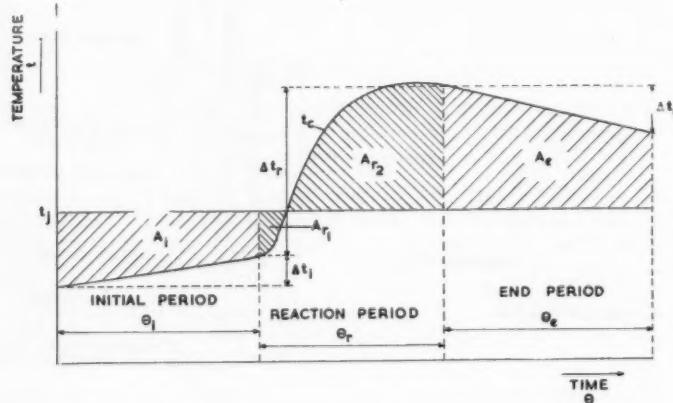


Fig. III—Typical calometric temperature-time curve obtained with a slow exothermic reaction

### Initial period:

$$(W + g.c_p) \Delta t_i = Q_{Fi} + Q_{fi} = F.A_i + f.\theta_i \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (3)$$

where  $g.c_p$  is a correction to the heat capacity of the calorimeter assigned to the presence of the reactants in the reaction vessel.

End period:

$$(W + g.c_p). \Delta t_e = Q_{Fe} + Q_{fe} = F.A_e - f.\theta_e \dots \dots \dots \dots \dots \quad (4)$$

Reaction period:

$$(W + g.c_p). \Delta t_r = Q_r - Q_{Fr} + Q_{fr} = Q_r - F.(A_{r2} - A_{r1}) + f.\theta_r \dots \dots \quad (5)$$

where,  $Q_r$  = heat effect of the reaction taking place in the reaction vessel, cal

$W$  = heat capacity of the completely assembled calorimeter unit, cal/°C

$g$  = total weight of reaction mixture, g

$c_p$  = heat capacity of reaction mixture, cal/°C g

$\Delta t$  = change in temperature of the calorimeter unit, °C

$A$  = graphically determined value of the integral in eqn (1), °C min

and the subscripts i, e and r apply to the initial, end and reaction periods respectively.

The heat effect,  $Q_r$ , being known, the three calibration constants  $W$ ,  $F$  and  $f$  can be evaluated from equations (3), (4) and (5).

In the calibration of the unit, equations (3) and (4) were derived from temperature/time plots obtained on fairly long experimental runs in the absence of any reactants. Consequently the correction term  $g.c_p$  was not applicable. Equation (5) was derived from calorimetric data obtained when dissolving ammonium nitrate in water.\*

Two independent sets of such calibration data were used and found to give identical results. The following values for the calibration constants were obtained:

$$W = 392.5 \text{ cal/}^{\circ}\text{C}, F = 0.928 \text{ cal/min } ^{\circ}\text{C and } f = 0.040 \text{ cal/min.}$$

To test the suitability of the calorimeter for measuring heats of reaction the heat effect of the reaction between calcium hydroxide and nitric acid was determined and compared with the value calculated from the heat of formation values of the compounds involved in the reaction. The results of these tests are given in Table I.

TABLE I

*Experimental and calculated heat effects of the stoichiometric reaction between nitric acid (aq) and calcium hydroxide (s) at 25°C.*

Calcium hydroxide + 30% nitric acid									
Weight reactants (g)		g.c <sub>p</sub> (cal/°C)	Δt <sub>r</sub> (°C)	A <sub>r2</sub> - A <sub>r1</sub> (min °C)	θ <sub>r</sub> (min)	Q <sub>r</sub> (cal)	ΔH <sub>r</sub> (kcal/mole)	Experi- mental (mean)	Calcu- lated
Ca(OH) <sub>2</sub> (s)	HNO <sub>3</sub> (aq)								
1.1789	6.7033	4.7	1.304	8.00	30	524.2	-32.9	-32.7	-32.5
1.2609	7.1609	5.1	1.362	12.08	20	551.9	-32.4		
1.2188	6.9257	4.9	1.326	12.96	20	538.2	-32.7		

Calcium hydroxide + 40% nitric acid									
1.6140	6.8660	4.0	1.845	8.56	20	738.8	-33.9	-33.8	-33.6
1.4904	6.3491	3.7	1.733	-3.04	20	683.0	-33.8		
1.4988	6.3747	3.7	1.709	7.04	20	682.9	-33.7		

\* As ammonium nitrate has a negative heat of solution the last term in equation (5) should be written with a negative sign when absolute values are used.

$Q_r$ , in Table I, was calculated from the experimental data by equation (5) in the following form:

$$Q_r = (W + g.c_p) \cdot \Delta t_r + F \cdot (A_{r2} - A_{r1}) - f \cdot \theta_r \dots \dots \dots \dots \dots \dots \quad (6)$$

The calculated heats of reaction per mole of solid reactant ( $\Delta H_r$ ) correspond to the following reaction:

*	$\text{Ca(OH)}_2 \text{ (s)}$	$+ 2\text{HNO}_3 \text{ (aq)}$	$= \text{Ca(NO}_3)_2 \text{ (aq)}$	$+ 2\text{H}_2\text{O (l)}$
$\Delta H_f(30\% \text{HNO}_3)$	-235.80	-48.858	-229.39	-68.317
$\Delta H_f(40\% \text{HNO}_3)$	-235.80	-48.336	-229.45	-68.317

Table I shows close agreement between the calculated and experimental values of the heat of reaction.

#### RESULTS

With the calorimeter unit described above, calorimetric data on the reactions between hydroxy-, fluor- and chlorapatites and nitric acid of 20% and 30% concentration (w/w), respectively, were obtained. From the experimental data the amounts of heat evolved during these reactions were calculated by equation (6). The heat of reaction values thus found were subsequently used in calculating the heats of formation of the apatites by making up the heat balance on the chemical reactions involved. These reactions were taken to be as follows:

$\text{Ca(OH)}_2 \cdot 3\text{Ca}_3(\text{PO}_4)_2 \text{ (s)}$	$+ 14 \text{ HNO}_3 \text{ (aq)}$	$+ \text{H}_2\text{O (l)}$	$=$	
		-49.132 (20%)		
$\Delta H_f$		-68.317		
		-48.858 (30%)		
$7\text{Ca}(\text{NO}_3)_2 \text{ (aq)}$	$+ 3\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O (s)}$			
-229.29	-816.82	-816.82*		
-229.41		-229.41		
$\text{CaF}_2 \cdot 3\text{Ca}_3(\text{PO}_4)_2 \text{ (s)}$	$+ 14 \text{ HNO}_3 \text{ (aq)}$	$+ 3\text{H}_2\text{O (l)}$	$=$	
		-49.132 (20%)		
$\Delta H_f$		-68.317		
		-48.858 (30%)		
$7\text{Ca}(\text{NO}_3)_2 \text{ (aq)}$	$+ 3\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O (s)}$	$+ 2\text{HF (aq)}$		
-229.29	-816.82	-75.685		
-229.41		-229.41		
$\text{CaCl}_2 \cdot 3\text{Ca}_3(\text{PO}_4)_2 \text{ (s)}$	$+ 14 \text{ HNO}_3 \text{ (aq)}$	$+ 3\text{H}_2\text{O (l)}$	$=$	
		-49.132 (20%)		
$\Delta H_f$		-68.317		
		-48.858 (30%)		
$7\text{Ca}(\text{NO}_3)_2 \text{ (aq)}$	$+ 3\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O (s)}$	$+ 2 \text{HCl (aq)}$		
-229.29	-816.82	-39.707		
-229.41		-229.41		
		-39.597		

X-ray and chemical analysis showed that, in accordance with the above equations, the solid phase in the final product consisted entirely of mono-calcium orthophosphate mono-hydrate. Since the reaction temperature was only 25°C and the system contained an ample amount of water, it has been assumed that the hydrofluoric and hydrochloric acids were retained in the final product as aqueous solutions.

\* These and subsequent heat of formation values, with the exception of the value for mono-calcium phosphate mono-hydrate, were taken from Reference 5.

The calorimetric date and the quantities calculated from these are summarised in Table II.

TABLE II

*Heats of formation of apatites (s) calculated from experimental heats of reaction with nitric acid (aq) at 25°C.*

Solid reactant	Apatites + 20% nitric acid								
	Weight reactants (g)		g.c.p. (cal/ °C)	$\Delta t_r$ (°C)	$A_{r2}-A_{r1}$ (min °C)	$\theta_r$ (cal)	$Q_r$ (cal)	$\Delta H_r$ (kcal/ mole)	$\Delta H_f$ (kcal/ mole)
	Apatite	HNO <sub>3</sub> (aq)							
hydroxy-apatite	1.5464	6.7937	5.4	0.257	7.34	50	107.3	-69.7	-3229.7
fluor-apatite	1.7474	7.6287	6.1	0.215	9.30	50	92.3	-53.3	-3260.8
chlor-apatite	1.8186	7.7078	6.0	0.292	9.69	50	123.4	-70.7	-3171.5

Solid reactant	Apatites + 30% nitric acid								
	Weight reactants (g)		g.c.p. (cal/ °C)	$\Delta t_r$ (°C)	$A_{r2}-A_{r1}$ (min °C)	$\theta_r$ (cal)	$Q_r$ (cal)	$\Delta H_r$ (kcal/ mole)	$\Delta H_f$ (kcal/ mole)
	Apatite	HNO <sub>3</sub> (aq)							
hydroxy-apatite	2.3147	6.7901	4.6	0.416	2.69	50	165.9	-72.0	-3232.0
fluor-apatite	2.3731	6.9186	4.6	0.290	16.52	50	128.7	-54.7	-3264.0
chlor-apatite	1.8900	5.3395	3.1	0.323	9.38	50	134.7	-74.3	-3172.3

In all cases the apatite/acid reactions were taken to be complete within fifty minutes since extension of this period produced the same final result.

The experimental data given in Table II are averages of corresponding data obtained on two single determinations in each case. The differences in the single determinations of  $\Delta H_r$  amounted to 1.0, 1.4 and 1.2 kcal/mole in the case of 20% nitric acid, and 1.2, 0.6 and 2.0 kcal/mole in the case of 30% nitric acid for hydroxy-, fluor- and chlorapatite respectively.

The following heats of formation of the apatites are the mean of the values found from the reaction with 20% and 30% nitric acid, with an estimated accuracy of approximately 0.07%:

$$\begin{array}{ll} \text{hydroxyapatite} & : \Delta H_f = -3231 \text{ kcal/mole} \\ \text{fluorapatite} & : \Delta H_f = -3262 \text{ kcal/mole} \\ \text{chlorapatite} & : \Delta H_f = -3172 \text{ kcal/mole} \end{array}$$

As mentioned earlier the synthetic apatites used in these experiments contained impurities, which in the case of hydroxy- and chlorapatites may amount up to 1.5% and in the case of fluorapatite up to 3%. The methods of preparing these apatites are likely to give rise to the following impurities in the final products: calcium pyrophosphate in hydroxyapatite, calcium fluoride and tricalcium phosphate in fluorapatite, and calcium chloride and tricalcium phosphate in chlorapatite. It can be calculated that the maximum bias in the experimental heats of reaction ( $\Delta H_r$ ),

arising from these impurities is +0.5, +1.0 and +1.8 kcal/mole for hydroxy-, chlor- and fluorapatite respectively. The heat of formation values given in Table II would then become greater by the same amounts.

Thanks are due to Mr. C. Pronk, who assembled the calorimeter unit and the auxiliary equipment and carried out the experiments with the necessary care, and to Messrs. J. A. Dreyer and J. Mulder for preparing the synthetic apatites. Messrs. African Explosives and Chemical Industries, Limited, are thanked for permission to publish this paper.

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#### REFERENCES

- <sup>1</sup> Hayek and Stadtmann, *Angew. Chem.*, 1955, **67**, 327.
- <sup>2</sup> Egan, Wakefield and Elmore, *J. Amer. Chem. Soc.*, 1951, **73**, 5581.
- <sup>3</sup> Torok, *Agrohemia es Talajtarr*, 1955, **4**, 355.
- <sup>4</sup> Wallaeys, *Ann. Chim. (France)*, 1952, **7**, 808.
- <sup>5</sup> National Bureau of Standards, "Selected Values of Chemical Thermodynamic Properties", Circular 500, 1952.
- <sup>6</sup> Egan, Wakefield and Elmore, *J. Amer. Chem. Soc.*, 1956, **78**, 1811.

THE STRUCTURE OF "α" AND "β" ETHYL AND METHYL  $\beta$ -BENZOYL-AMINOCROTONATES AND THE CHEMICAL CONSTITUTION AND CERTAIN REACTIONS OF THE PRODUCT FORMED FROM THEM BY THE ACTION OF PHOSPHORUS PENTACHLORIDE

by

R. J. FRIEDLAND and O. G. BACKEBERG

OPSOMMING

Die struktuur van die isomeriese etiel en metiel  $\beta$ -benzoëlaminokrotonate is bepaal en die struktuur van die produkte wat gevorm is by behandeling met fosforpentachloried vasgestel. Benary, wat heeleerste hierdie produk uit etielasetielsetaat berei het, het dit beskou as die ooreenkomsstige imidochloried. Staskun wat op sy beurt hierdie produk ondersoek het, het voorgestel dat dit etiel 1-chloro-3-metiel isokinolien-4-karboksilaat was. Dit is nou bewys dat dit etiel  $\alpha$ -chloro- $\beta$ -benzoëlaminokrotonaat is en die ooreenkomsstige metielverbinding sowel as die etiel-en metieljodiumverbindings is berei. Verskeie verwante tussenverbindingen is ook berei.

Die hidrolise van etiel en metiel  $\alpha$ -chloro- $\beta$ -benzoëlaminokrotonate tot die ooreenkomsstige suur deur middel van kaliumkarbonaat word beskryf.

Die hidrolise van die esters met natriumhidroksied lei tot die formasie van 2-feniel-4-metiel-oksasool-5-karboksilsuur.

SUMMARY

The fine structure of the isomeric ethyl and methyl  $\beta$ -benzoylaminocrotonates has been determined and the structure of the products formed from them by the action of phosphorus pentachloride has been elucidated. Benary, who first prepared the product from ethyl acetoacetate, regarded it as the corresponding imidochloride; Staskun, who reinvestigated the compound considered that it was ethyl 1-chloro-3-methylisquinoline-4-carboxylate. It has now been shown to be ethyl  $\alpha$ -chloro- $\beta$ -benzoylaminocrotonate and the corresponding methyl as well as the ethyl and methyl iodo-compounds have been prepared. In addition, several related intermediate compounds have also been prepared.

The hydrolysis of ethyl and methyl  $\alpha$ -chloro- $\beta$ -benzoylaminocrotonates to the corresponding acid by means of potassium carbonate is described.

The hydrolysis of the esters with sodium hydroxide leads to the formation of 2-phenyl-4-methyloxazole-5-carboxylic acid.

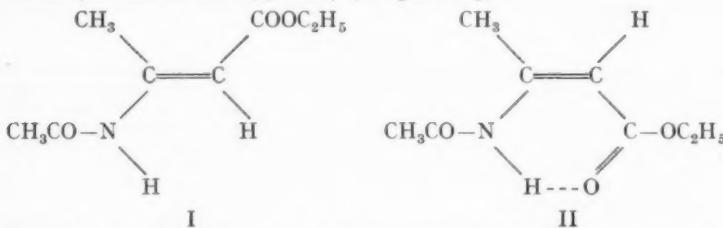
Benary<sup>1</sup> found that ethyl  $\beta$ -aminocrotonate, prepared by the action of ammonia on ethyl acetoacetate, formed two isomeric products when it was allowed to react with benzoyl chloride, a labile compound, m.p. 95-96° and a stable compound, m.p. 46-48°, which he designated as the "α" and "β" forms respectively. The corresponding acetyl compound was prepared (i) by Canzoneri and Spica<sup>2</sup> by the action of acetamide on ethyl acetoacetate in the presence of aluminium chloride; (ii) by Collie<sup>3</sup> from the amine and acetic anhydride and (iii) by Benary from the amine and acetyl chloride; in addition he obtained a higher melting, labile isomer. Benary also prepared the stable "β" benzoyl derivative of the amine referred to above from benzamide according to the method of Canzoneri and Spica.

Benary suggested three possibilities for the nature of the isomerism of the acetyl and benzoyl derivatives:—

- (i) The isomers might be derivatives of a crotonate or a butyrate (R=Me or Ph) i.e.,  $\text{CH}_3\text{C}(\text{NHCOR})\text{CH}(\text{COOEt})_2$  or  $\text{CH}_3\text{C}(\text{N.COR})\text{CH}_2\text{COOEt}$ .
- (ii) A cis-trans type of isomerism about the double bond of the crotonate.

(iii) Isomerism involving the nitrogen atom in the butyrate structure, giving syn- and anti-forms; he considered this type of isomerism to be excluded because both benzoyl isomers formed the same product by the action of phosphorus pentachloride.

Twenty-one years after Benary's publication, physico-chemical methods were applied to the elucidation of the structure of compounds formed by ethylacetoacetate with ammonia and primary and secondary amines. The molecular refractions of some of these compounds were measured by von Auwers and Susemihl<sup>4</sup> and Glickman and Cope<sup>5</sup> showed by means of ultra-violet absorption spectra that these compounds were derivatives of ethyl  $\beta$ -aminocrotonate rather than of the  $\beta$ -ketimidoxybutyrate. Von Auwers and Wunderling<sup>6</sup> extended this work by measuring the specific exaltations of the molecular refractions of the isomeric  $\beta$ -benzylamino-,  $\beta$ -acetylamino- and  $\beta$ -benzoylamino-derivatives of ethyl acetoacetate. In all these cases the structure was once more found to be that of a derivative of crotonic rather than of butyric acid. Clearly then, the " $\alpha$ " and " $\beta$ " isomers referred to must correspond with the two possible arrangements of the various groups in relation to the ethylenic double bond of crotonic acid, and the fine structure of these compounds was worked out by Grob<sup>7</sup> in the case of  $\beta$ -acetylaminocrotonate. Although he observed that chemical methods such as cyclisation or ring fission were of no avail in determining the structure of the two isomers, he found that in addition to ultra-violet absorption spectra, the use of the "wet" melting point method, originated by Baker<sup>8</sup> and also used by Hunter<sup>9</sup>, served to identify the isomers. Grob considered that the two structures of the " $\alpha$ " and " $\beta$ " isomers were (I) and (II) respectively,



that is, ethyl  $\beta$ -acetylaminocrotonate (I) and ethyl  $\beta$ -acetylaminocrotonate (II); they are thus derivatives of isocrotonic and crotonic acid respectively. It will be noted that the structure (II) contains a chelate six-membered ring formed by hydrogen bonding. Consequently, in polar solvents such compounds will be almost non-associated because of the inability of the -NH- and -CO- groups to form intermolecular hydrogen bonds. Such compounds will be more soluble than the non-chelated and consequently associated form (I) and they will have lower melting points because of the smaller intermolecular forces in the solid state. Furthermore, it may be expected that the chelate form will be the more stable. When the melting point of these isomers is determined in the presence of water, an important difference between (I) and (II) appears. In the latter case the depression will result from the interaction between water and one molecular species only, since there will be very little association of (II) in the presence of the polar water molecules. In the former case, however, association will occur in the presence of water, so that a number of organic molecular species will be present and there will be a considerable depression of the melting point by the mutual interaction of the various molecular species and water; the depressions recorded by Grob for (I) and (II) were 30° and 4° respectively.

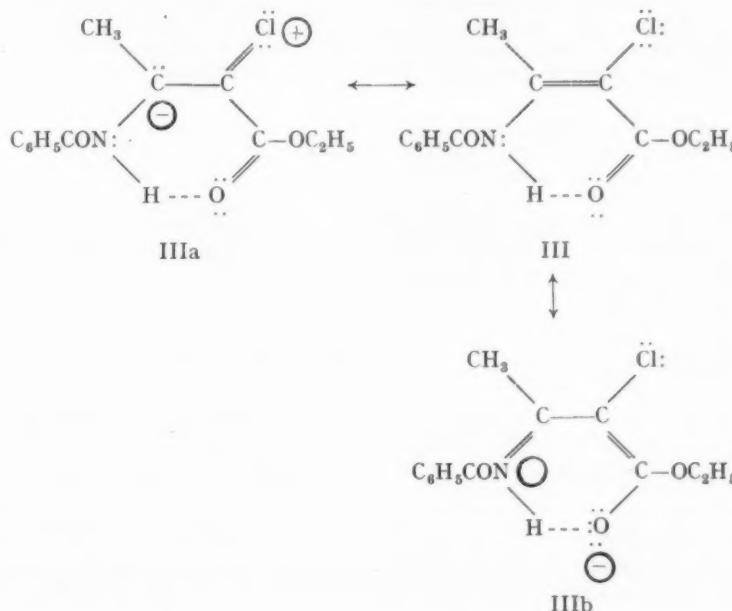
The authors determined the ultra-violet absorption spectra and applied the "wet" melting point method to the isomeric pairs of  $\beta$ -benzoylamino-derivatives

of ethyl and methyl acetoacetate and obtained similar results for the stable lower-melting and labile higher-melting isomers.

Benary examined the reaction of both isomers of ethyl  $\beta$ -benzoylaminocrotonate with phosphorus pentachloride and reported that they formed the same imidochloride which he crystallised from dilute alcohol. That such a reactive type of compound could be crystallised from this solvent without decomposition appeared so improbable to Staskun<sup>10</sup> that he suggested an alternative structure for it, namely ethyl 1-chloro-3-methylisoquinoline-4-carboxylate. This compound has been further examined by the authors and shown to be *ethyl  $\alpha$ -chloro- $\beta$ -benzoylaminocrotonate*. This has been confirmed (i) by its synthesis from ethyl  $\alpha$ -chloroacetoacetate and benzamide; (ii) by its preparation from the reaction between ethyl  $\beta$ -benzoylaminocrotonate and sulphuryl chloride; (iii) by its degradation to chloroacetone and benzoic acid. The following are the analytical data for the formulae of this compound as proposed by Benary, by Staskun and by the authors:—

	C		H		N		Cl	
	Calc. Found							
Benary: $C_{13}H_{14}O_2NCl$ . . . . .	62.0	—	5.6	—	5.6	—	14.1	13.9
Staskun: $C_{13}H_{13}O_2NCl$ . . . . .	62.5	—	4.8	—	5.6	5.9	14.2	—
Authors: $C_{13}H_{14}O_2NCl$ . . . . .	58.3	58.3	5.2	5.2	5.2	5.3	13.3	13.1

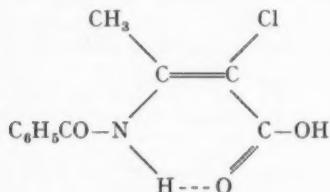
This compound does not appear to form two geometrical isomers and from its ultra-violet and infra-red spectra as well as from its "wet" melting point it is considered to be ethyl  $\alpha$ -chloro- $\beta$ -benzoylaminocrotonate (III) and its stability, referred to later, could be ascribed to the following mesomeric forms:—



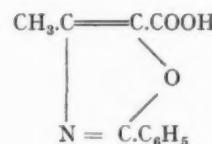
The *methyl ester* as well as the *methyl* and *ethyl iodo-compounds* corresponding to (III) have also been prepared. In addition, the following compounds, not previously described, were prepared:— *methyl β-benzoylaminocrotonate* and *iso-crotonate*; *methyl α-chloroacetoacetate*; *methyl α, α-dichloroacetoacetate*.

In an attempt to elucidate the structure of the compound (III) Staskun subjected it to mild and strong alkaline hydrolysis and obtained two different acids which, in keeping with his view of the isoquinoline structure of the *α*-chloro-compound, he considered to be 1-chloro-3-methyloquinoline-4-carboxylic acid and the corresponding 1-hydroxy-derivative respectively.

These two hydrolysis products have been re-examined and found to be *α-chloro-β-benzoylaminocrotonic acid* (IV) and *2-phenyl-4-methyloxazale-5-carboxylic acid* (V) respectively. Because of the very similar ultra-violet absorption spectra of the acid (IV) and its esters and the small depression of the "wet" melting point, it is considered to have the same type of chelate structure.



IV

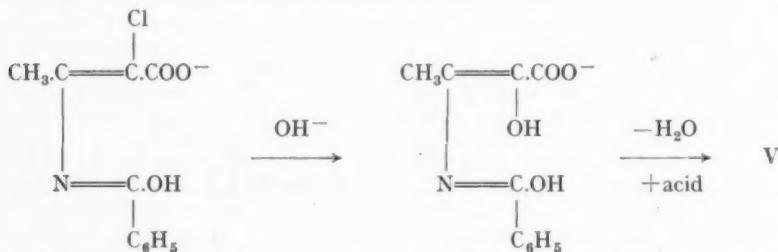


V

The conversion of (IV) into (V) would require its rearrangement about the ethylenic double bond into the isocrotonic acid followed by ring-closure. This type of rearrangement could be accounted for by assuming that an *SN* reaction under the influence of the strongly nucleophilic hydroxide ion is involved:—



This would mean that *α*-hydroxy-*β*-benzoylaminocrotonic acid is probably an intermediate product, so that the conversion could be formulated as follows, the benzoyl group reacting in the tautomeric enimic form:—



The *α*-chlorine atom which is part of a chlorovinyl grouping would be expected to be inert because of the stabilisation of this grouping by the mesomeric forms (III)

and (IIIa) and together with the chelate structure must account for the unusual stability of the acid (IV) and its esters. Thus, while the  $\beta$ -benzoylamino esters are readily hydrolysed to benzamide by boiling with dilute acids, the  $\alpha$ -chloro compounds are unaffected by this treatment. The inertness of the  $\alpha$ -chloro atom in these crotonic acid derivatives is further shown by the fact that they are largely unaltered by treatment with zinc and acetic acid, stannous chloride and hydrogen chloride, ammonia, potassium cyanide, thionyl chloride, sodium iodide and sodium.

The structure of the acid (V) was confirmed by its synthesis from  $\alpha$ -chloroacetacetate by the method of Cornforth and Cornforth<sup>11</sup>; this synthesis is analogous to that of 2-phenyl-4-methylthiazole-5-carboxylic acid from ethyl  $\alpha$ -chloro-acetoacetate and thiobenzamide<sup>12</sup>. The acid (V) was decarboxylated to the known 2-phenyl-4-methyloxazole<sup>13</sup>.

#### EXPERIMENTAL

(Melting points are uncorrected, halogen determinations were by the method of Schöniger<sup>14</sup> and ultra-violet spectra were determined in 96% ethanol solution.)

*Methyl  $\alpha$ -chloroacetacetate.* (Compare Macbeth's modification<sup>15</sup> of Allihn's procedure<sup>16</sup>). Sulphuryl chloride (80.3 g, 1.06 moles) was added dropwise with shaking to methyl acetoacetate (65 g) cooled in ice. After effervescence had ceased, the product was heated on the water-bath for one hour to complete the reaction. After cooling, ether (150 ml) was added and the solution washed well with water and dried over magnesium sulphate. The ether was removed and the product distilled under reduced pressure; on redistillation, the ester (42.1 g, 50%) was obtained as a faintly yellow, lachrymatory liquid which gave an intense violet colour with ferric chloride, b.p. 97°/30mm, 195.5°/625 mm;  $n_D^{22}$  1.4470;  $d^{22.5}$  1.2468 (Found: Cl, 24.1, 24.2.  $C_5H_7O_3Cl$  requires Cl, 23.6%).

The known ethyl ester was similarly prepared in 65% yield.

*Methyl  $\alpha$ ,  $\alpha$ -dichloroacetacetate* was prepared similarly in 58% yield, using double the proportion of sulphuryl chloride; pale yellow lachrymatory liquid, b.p. 101°/30 mm, 187°/622 mm;  $n_D^{22.5}$  1.4519;  $d^{23}$  1.3470 (Found: Cl, 38.4, 38.3.  $C_5H_6O_3Cl_2$  requires Cl, 38.4%).

*Methyl  $\beta$ -benzoylaminoisocrotonate.* Benzoyl chloride (56 g, 1 mole) dissolved in absolute ether (60 ml) was added dropwise during 30 minutes, with vigorous shaking, to a solution of methyl  $\beta$ -aminocrotonate<sup>17</sup> (41.2 g) dissolved in a mixture of dry pyridine (46 g) and absolute ether (230 ml). The mixture was kept cold in ice and salt throughout the reaction and care was taken to avoid any local rise in temperature during addition of the benzoyl chloride. A precipitate gradually formed and after the addition of the benzoyl chloride the mixture was allowed to stand in the freezing mixture for a further two hours; the solid was then filtered off, washed well with ether, then with water to remove pyridine hydrochloride, followed by sodium bicarbonate solution and water. The product (20 g, 25%) crystallised from dilute alcohol, m.p. 119°;  $\lambda_{\max}^{276m\mu}$ ,  $\log\epsilon$  4.26;  $\lambda_{\max}^{230m\mu}$ ,  $\log\epsilon$  3.99 (Found: N, 6.3.  $C_{12}H_{13}O_3N$  requires N, 6.4%).

*Methyl  $\beta$ -benzoylaminocrotonate.* When the ether was removed from the combined ethereal filtrate and washings above, a yellow viscous oil was obtained from which impure isocrotonate (12 g), m.p. 110-115°, separated on cooling; this was filtered off and the filtrate cooled in the ice-chest for several days when crystalline material (12.3 g) separated. This was washed with sodium bicarbonate solution and water and recrystallised from dilute alcohol to give the pure isomeric  $\beta$ -benzoylaminocrotonate, (6g, 8%) small, colourless needles, m.p. 62-63°;  $\lambda_{\max}^{285m\mu}$ ,  $\log\epsilon$  4.24;  $\lambda_{\max}^{233m\mu}$ ,  $\log\epsilon$  4.13 (Found: N, 6.3%.  $C_{12}H_{13}O_3N$  requires N, 6.4%).

The above isocrotonate was converted into the stable isomer by dissolving in warm glacial acetic acid and leaving overnight. On pouring into water, the product which separated was crystallised from dilute alcohol, m.p. 62-63°, unaltered by admixture with the crotonate described above.

For preparative purposes the stable  $\beta$ -benzoylamino-esters were best prepared in one operation, illustrated by the following modification of Benary's procedure:— Benzamide (100 g) methyl acetoacetate (192 g, 2 moles) and powdered aluminium chloride (20 g) were heated on the water-bath for 8 hours with exclusion of atmospheric moisture. The excess methyl acetoacetate was removed by suitable heating under reduced pressure. The oily residue solidified on stirring with water and was washed well with dilute hydrochloric acid to remove aluminium chloride, giving crude dry product (116-6g), m.p. 62-63° after crystallisation from dilute alcohol.

*The action of phosphorus pentachloride on ethyl and methyl  $\beta$ -benzoylamino-crotonate.* The product (III), prepared according to the method of Benary, was obtained in 63% yield, m.p. 99°, after crystallisation from dilute alcohol;  $\lambda_{\text{max}}$  304m $\mu$ ,  $\log \epsilon$  4.17;  $\lambda_{\text{max}}$  238m $\mu$ ,  $\log \epsilon$  3.98 (Found: C, 58.3; H, 5.2; N, 5.3; Cl, 13.1, 13.1; M (Rast, camphor), 252.  $\text{C}_{13}\text{H}_{14}\text{O}_3\text{NCl}$  requires C, 58.3; H, 5.2; N, 5.2; Cl, 13.3%; M, 267.5).

The infra-red spectrum was determined on a 3.28% w/w solution in carbon disulphide and the following bands (in cm<sup>-1</sup>) were observed:—

- (i) 3232, 3175: Intramolecular hydrogen-bonded N-H stretching modes;
- (ii) 1691: Amide I band due to C=O stretching vibration;
- (iii) 1651: Possibly chelated C=O stretching vibration;
- (iv) 1250, 1159: Ester C=O stretching band;
- (v) 703: C-Cl stretching frequency.

*Methyl  $\alpha$ -chloro- $\beta$ -benzoylamino-crotonate.* Both methyl  $\beta$ -benzoylamino-crotonate and isocrotonate formed the same product, in 70% yield, on treatment with phosphorus pentachloride; it crystallised from dilute alcohol in small, colourless needles, m.p. 90°;  $\lambda_{\text{max}}$  303m $\mu$ ,  $\log \epsilon$  4.24;  $\lambda_{\text{max}}$  237m $\mu$ ,  $\log \epsilon$  4.05 (Found: N, 5.6; Cl, 14.0, 14.3.  $\text{C}_{12}\text{H}_{12}\text{O}_3\text{NCl}$  requires N, 5.5; Cl, 14.0%).

*Condensation of benzamide with  $\alpha$ -chloroacetoacetic esters in the presence of aluminium chloride.* Benzamide (5 g) and methyl  $\alpha$ -chloroacetoacetate (12.5 g, 2 moles) together with powdered aluminium chloride (1 g) were heated on the water-bath for 6 hours with exclusion of atmospheric moisture and left overnight. On pouring into water a pasty solid separated from which methyl  $\alpha$ -chloro- $\beta$ -benzoylamino-crotonate (1.25 g, 12%) was obtained after crystallisation from dilute alcohol, m.p. 90°, unchanged on admixture with the compound described above. Ethyl  $\alpha$ -chloroacetoacetate similarly formed the compound (III) in 6% yield, m.p. 99°, identical (m.p. and mixed m.p.) with the product described by Benary.

*Action of sulphuryl chloride on ethyl  $\beta$ -benzoylamino-crotonate.* Sulphuryl chloride (1.7 g, 1.5 moles) dissolved in absolute ether (10 ml) was added dropwise with shaking to ethyl  $\beta$ -benzoylamino-crotonate (2 g) dissolved in absolute ether (25 ml). The ether was removed at room temperature under reduced pressure and the gummy residue, which solidified on treatment with water, was crystallised from dilute alcohol, giving a product (1.02 g, 44%), m.p. 99°, identical (m.p. and mixed m.p.) with the compound (III). The corresponding methyl chloro-ester was similarly prepared in 56% yield.

That sulphuryl chloride replaces hydrogen on the  $\alpha$ -carbon atom was shown by the fact that under similar conditions it did not react with ethyl  $\alpha$ -methyl- $\beta$ -benzoyl-aminocrotonate (a compound first described by Staskun).

*Degradation of ethyl  $\alpha$ -chloro- $\beta$ -benzoylaminocrotonate.* The compound (III) (0.3 g) was refluxed with 50% sulphuric acid (6 ml) for 15 minutes. On cooling, benzoic acid, m.p. 122°, crystallised out. The filtrate contained chloroacetone, isolated as its 2,4-dinitrophenylhydrazone, m.p. 124-126°, unaltered on admixture with an authentic specimen.

*Ethyl  $\alpha$ -iodo- $\beta$ -benzoylaminocrotonate.* Ethyl  $\beta$ -benzoylaminocrotonate (9.18 g) was dissolved in ethanol (24 ml) and added to a solution of iodine (10 g, 1 mole) in ethanol (120 ml) to which N ethanolic sodium hydroxide (39.4 ml, 1 mole) had been added. The product separated almost immediately and after crystallisation from alcohol gave pure compound (12 g, 85%), m.p. 117° (Found: I, 35.2, 35.3; N, 3.9.  $C_{13}H_{14}O_3NI$  requires I, 35.4; N, 3.9%). It decomposed in solution as well as on keeping for some time.

The same procedure, using methyl  $\beta$ -benzoylaminocrotonate and methanol as solvent—this was necessary to prevent transesterification—gave *methyl  $\alpha$ -iodo- $\beta$ -benzoylaminocrotonate* in 78% yield, m.p. 118°;  $\lambda_{\text{max}}$  318m $\mu$ ,  $\log \epsilon$  4.18;  $\lambda_{\text{max}}$  239m $\mu$ ,  $\log \epsilon$  4.08 (Found: I, 37.1, 37.4; N, 4.05.  $C_{12}H_{12}O_3NI$  requires I, 36.8; N, 4.1%). Like the ethyl ester described above, it was not very stable. That transesterification does take place was shown by the fact that iodination of the methyl ester in ethanol, using ethanolic sodium hydroxide, gave almost pure ethyl  $\alpha$ -iodo-derivative, m.p. and mixed m.p. 116°, after one crystallisation from ethanol.

*$\alpha$ -Chloro- $\beta$ -benzoylaminocrotonic acid (IV).* The ethyl ester (0.73 g) was refluxed for 80 minutes with potassium carbonate (1.5 g) dissolved in 30% aqueous alcohol (50 ml). The solution was left overnight, filtered and acidified. The product (0.49 g) crystallised from dilute alcohol in small colourless plates, m.p. 134-135° (dec.);  $\lambda_{\text{max}}$  293m $\mu$ ,  $\log \epsilon$  4.13;  $\lambda_{\text{max}}$  234m $\mu$ ,  $\log \epsilon$  4.04 (Found: C, 55.5; H, 4.6; N, 6.1, 6.0; Cl, 14.6, 14.6. Equivalent weight, 233.  $C_{11}H_{10}O_3NCl$  requires C, 55.1; H, 4.2; N, 6.1; Cl, 14.8%. Equivalent weight, 239.5).

The iodo-esters could not be similarly hydrolysed under the above conditions; they were largely decomposed and formed a small quantity of the acid (V).

The inertness of the  $\alpha$ -chloro atom in the acid (IV) and its esters (on which the reactions were actually carried out) is illustrated in the following reactions in which these compounds were recovered largely unchanged:—(i) by boiling with water or 10% sulphuric acid for one hour; the hydrolysis with 50% sulphuric acid has already been described; (ii) by treatment with zinc and acetic acid (Campbell)<sup>18</sup>; (iii) by treatment with stannous chloride and hydrogen chloride in ether (Stephen)<sup>19</sup>; (iv) by allowing to stand at room temperature with concentrated ammonia for one month; on boiling for four hours with aniline in glacial acetic acid a small quantity of ester was recovered, but most of it was decomposed; (v) by boiling for five hours with potassium cyanide in 50% alcoholic solution; if the alcohol was different from that of the ester group, transesterification took place; (vi) by boiling with thionyl chloride for 75 minutes; heating with phosphorus pentachloride in phosphoryl chloride solution decomposed the esters and an imidochloride did not appear to be formed; (vii) by boiling for 12 hours with sodium iodide in acetone or alcoholic solution (Finkelstein)<sup>20</sup>; (viii) by boiling with sodium for five hours in xylene solution; (ix) by boiling for one hour with the sodium derivative of  $\beta$ -benzoylaminocrotonic ester in xylene solution; boiling with sodium ethylate in solution led to the formation of the acid (V).

*2-Phenyl-4-methyloxazole-5-carboxylic acid (V).* (i) Methyl  $\alpha$ -chloro- $\beta$ -benzoylaminocrotonate (10 g) was refluxed with 6% aqueous potassium hydroxide (170 ml, 4 moles) for 40 minutes. Acidification of the solution gave material (2.77 g, 35%) which crystallised from dilute alcohol in colourless needles, m.p. 240-242° (dec.);

$\lambda_{\text{max}}$  283m $\mu$ ,  $\log \epsilon$  4.28 (Found: C, 65.0; H, 4.4; N, 7.3, 7.25; M (Rast, camphor) 211; Equivalent weight, 198.  $\text{C}_{11}\text{H}_9\text{O}_3\text{N}$  requires C, 65.0; H, 4.4; N, 6.9%. M and Equivalent weight, 203). Ether extraction of the filtrate yielded benzoic acid. (ii) The acid was formed in good yield from the  $\alpha$ -iodo-esters by boiling the ester (2 g) with N ethanolic sodium hydroxide (20 ml) for 45 minutes.

(iii) Synthesis from ethyl  $\alpha$ -chloroacetoacetate<sup>11</sup>:—

A mixture of benzoic acid (80 g), ammonium benzoate (45 g) and ethyl  $\alpha$ -chloroacetoacetate (10 g) was heated under reflux in an oil-bath for 4½ hours at 145°C. The dark cake which formed on cooling was warmed with excess sodium carbonate and filtered from a small quantity (2 g) of brown solid. The filtrate was extracted with ether and the ether removed to leave a gummy residue (approximately 2 g) from which, on crystallisation from dilute alcohol, a small quantity of colourless needles, m.p. 195-197° was obtained. The mother liquor from these crystals was boiled with 10% sodium hydroxide for 15 minutes and acidified when the acid (V) (1 g) was obtained, m.p. 240-242° (dec.) after crystallisation from dilute alcohol, unaltered by admixture with the compound described above.

*Ethyl 2-phenyl-4-methylglyoxaline-5-carboxylate.* The compound, m.p. 195-197°, proved to be identical with the brown solid referred to above; after two further recrystallisations from dilute alcohol, it had m.p. 203-204° (Found: N, 12.3.  $\text{C}_{13}\text{H}_{14}\text{O}_2\text{N}_2$  requires N, 12.2%). It was sparingly soluble in ether, and is the expected by-product in this reaction<sup>11</sup>.

*2-Phenyl-4-methyloxazole.* The acid (V) (1g) mixed intimately with powdered soda-lime (2.5g) was heated with a small flame in a fusion tube drawn out to a 1 mm capillary. The distillate was extracted with ether and the extract dried with calcium chloride. After removal of the ether, the residue was distilled giving a colourless liquid with nicotine-like odour, which resinified on keeping; b.p. 211°/624 mm (Lewy<sup>13</sup> gives 238°/760 mm);  $\lambda_{\text{max}}$  271m $\mu$ ,  $\log \epsilon$  4.15.

The base did not form a picrate and was converted into its chloroplatinate, which crystallised as a hydrate from dilute hydrochloric acid in golden-brown needles, m.p. 189° (dec.) (Lewy gives 170° (dec.). (Found: Hydrate:  $\text{H}_2\text{O}$ , 5.2, 5.3.  $(\text{C}_{10}\text{H}_9\text{ON})_2\text{H}_2\text{PtCl}_6$ . 2 $\text{H}_2\text{O}$  requires  $\text{H}_2\text{O}$ , 4.7%).

*Anhydrous salt:* Pt, 26.4, 26.5; Cl, 29.1; 29.1.  $(\text{C}_{10}\text{H}_9\text{ON})_2\text{H}_2\text{PtCl}_6$  requires Pt, 26.8; Cl, 29.3%.

“*Wet*” melting point determinations. The sample was packed firmly to a depth of 5-10 mm into a capillary melting-point tube, about an equal column of water added through a hair-fine capillary from a drawn-out melting-point tube and the upper end of the tube sealed off. The following results were obtained:—

Substance	<i>m.p.</i>	" <i>Wet</i> " <i>m.p.</i>	Depression
Ethyl $\beta$ -benzoylaminocrotonate	48°	44-46°	3°
Ethyl $\beta$ -benzoylaminoisocrotonate	95-96°	78-83°	13°
Methyl $\beta$ -benzoylaminocrotonate	62-63°	57-58.5°	5°
Methyl $\beta$ -benzoylaminoisocrotonate	119°	94-100°	22°
Ethyl $\alpha$ -chloro- $\beta$ -benzoylaminocrotonate	99°	93-96°	4°
Methyl $\alpha$ -chloro- $\beta$ -benzoylaminocrotonate	90°	82-85°	6°
Ethyl $\alpha$ -iodo- $\beta$ -benzoylaminocrotonate	117°	111-114°	4°
Methyl $\alpha$ -iodo- $\beta$ -benzoylaminocrotonate	118°	111-114°	5°
$\alpha$ -Chloro- $\beta$ -benzoylaminocrotonic acid	134-135°(dec.)	133-134° (dec.)	1°

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#### REFERENCES

- 1 Benary, *Ber.*, 1909, **42**, 3912.
- 2 Canzoneri and Spica, *Gazz. Chim. It.*, 1884, **14**, 491.
- 3 Collie, *Ann.*, 1884, **226**, 294.
- 4 v. Auwers and Susemihl, *Ber.*, 1930, **63**, 1072.
- 5 Glickman and Cope, *J. Amer. Chem. Soc.*, 1945, **67**, 1017.
- 6 v. Auwers and Wunderling, *Ber.*, 1932, **65**, 79.
- 7 Grob, *Helv. Chim. Acta*, 1950, **33**, 1788.
- 8 Baker, *J. Chem. Soc.*, 1934, 1684.
- 9 Hunter, *Ann. Reports of the Chem. Soc.*, 1946, **43**, 145.
- 10 Staskun, *Ph.D. Thesis, University of the Witwatersrand*, 1954.
- 11 Cornforth and Cornforth, *J. Chem. Soc.*, 1953, 93.
- 12 Hubacher, *Ann.*, 1890, **259**, 237.
- 13 Lewy, *Ber.*, 1888, **21**, 2193.
- 14 Schöninger, *Mikrochim. Acta*, 1955, 123.
- 15 Macbeth, *J. Chem. Soc.*, 1923, **123**, 1125.
- 16 Allihn, *Ber.*, 1878, **11**, 567.
- 17 Conrad and Epstein, *Ber.*, 1887, **20**, 3055.
- 18 Campbell, *J. Org. Chem.*, 1946, **11**, 803.
- 19 Stephen, *J. Chem. Soc.*, 1925, **127**, 1874.
- 20 Finkelstein, *Ber.*, 1910, **43**, 1528.

## THE TRANSFORMATION OF WATER SOLUBLE PHOSPHATE INTO UNAVAILABLE PHOSPHATE IN EIGHT SOUTH AFRICAN SOILS

by

J. RIJKHEER

### OPSOMMING

Deur gebruik te maak van waterige oplossings van  $P^{32}$ -gemerkte monokalsiumfosfaat word aangetoon dat 'n water-oplosbare fosfaat by grond gevoeg, vinnig deur die labiele vorms van fosfaat in die grond versprei. Die gedeelte van die toegevoegde fosfaat wat toeganklik bly is gelyk aan die gedeelte van die corspronklike labiele grond-fosfaat wat toeganklik was.

### SUMMARY

By the use of  $P^{32}$ -labelled monocalcium phosphate solutions it has been shown that water soluble phosphate, when added to soil is quickly distributed throughout the labile forms of phosphate in the soil. The fraction of the added phosphate which remains available is equal to the fraction of the original labile phosphate which was available.

### INTRODUCTION

For efficient soil management the fate of fertiliser phosphate in a soil is as important a consideration as the phosphorous status of the soil. Since the end of the last century, when it was realised that the total phosphorous content of a soil is generally useless as a criterion of its phosphorus status, many biological, chemical and latterly, radiochemical techniques have been proposed for assessing the ability of soils to meet the phosphate requirements of crops. All such methods, purported to measure the amount of soil phosphorus that can be taken up by, or is available to plants, are empirical and cannot be expected to give more than an index of the availability of soil phosphorus to plants. It is generally accepted that their relative and absolute usefulness must ultimately be judged by the degree of correlation with field trials.<sup>1</sup>

Soil phosphate is known to exist in different forms which are not equally available to plants and phosphate additives are known to revert, with time, to similar forms.<sup>2</sup> This suggests that radioactive phosphorus could be used to trace the fate of fertiliser phosphate among the various categories of soil phosphate and at the same time give information about the phosphorus status of the soil. This has been the basis of many similar investigations. In techniques used in the past, workers have relied on isotopic exchange between soil phosphorus and its radioactive isotope in aqueous suspensions of soils to give a measure of the exchangeable soil phosphates<sup>3,4</sup>. In these investigations empirically determined periods were allowed for equilibration between soil and added phosphates in the systems used.

In the work reported here a combination of a radiochemical technique with some chemical extraction procedures which have been claimed to give a measure of the phosphorus status of soils, has been used to study the fate of fertiliser phosphate in soils under natural conditions. The interactions between soil and added fertiliser were allowed to proceed naturally until no further trend was observable in the amount of labelled phosphates extractable by the different methods used. In this manner the time at which equilibrium was attained between soil and fertiliser phosphate could be established with certainty.

TABLE I  
*Description of soils examined*

## EXPERIMENTAL

The soils used are listed in Table I, together with their chemical analyses, which include total phosphate,  $P_t$ , determined by perchloric acid digestion and the extractable phosphate,  $P_e$ , determined by several available methods, which are briefly described in Table II. All of the soils used were fine enough to pass through a 2 mm sieve.

TABLE II  
*Brief description of methods used*

Method	Reagents	Soil/Solution Ratio	Extraction Procedure
Bray's	Ammonium fluoride .. 0.03 N Hydrochloric acid to adjust to .. .. 0.1 N	1 : 7	Shake for 40 seconds—filter.
Olsen's	Sodium bicarbonate .. 0.5 N Sodium hydroxide to adjust pH to .. .. 8.5	1 : 20	Shake for 30 minutes—filter.
0.3 N HCl	—	2 : 5	Shake for 10 minutes—filter.
Saunders	Sodium hydroxide .. .. 0.1 N	1 : 50	Boil for 1 hour—filter.
Dyer's	Citric Acid .. .. 1% w/v	1 : 10	Shake for 30 minutes, stand overnight, shake for 30 minutes—filter.

4 Kg samples of these soils were treated with three consecutive 100 ml lots of  $P^{32}$ -labelled monocalcium phosphate solution containing sufficient fertiliser to increase the soil phosphate content by about 10 p.p.m.  $P_2O_5$ . The solution was added evenly by means of a fine spray to the soil spread out in a half inch thick layer. Each 100 ml addition was followed by thorough mixing of soil and fertiliser. Water was added to adjust the soil moisture level to "sticky point"—a consistency at which a kneaded mass of the plastic soil is just about to stick to a knife<sup>5</sup>. The soils were stored in open polythene beakers in a room maintained at 20°C and 80 per cent relative humidity. The moisture contents of the samples were kept fairly constant throughout the experiment. Representative subsamples of each soil were withdrawn for examination immediately after treatment and mainly at weekly intervals thereafter.

Each subsample was air-dried at 30-35°C for four hours. It was then subjected to the digestion and extraction procedures used for the determination of total and extractable phosphate. The solutions obtained were not, however, assayed chemically; they were, instead, subjected to radiometric measurements of their content of labelled fertiliser phosphate, using a 20th Century type M12 G.M. liquid counter. The ratio of extractable to total fertiliser phosphate,  $r$ , was calculated from the results. Subsampling was continued until equilibrium, according to the radiometric measurements, had for all practical purposes been established between soil and fertiliser phosphate.

## RESULTS

The results of the initial and equilibrium radiometric measurements are given in Table III. The table includes the approximate time,  $t$ , in days, in which virtual equilibrium between soil and fertiliser phosphate was attained; the value of  $t$  was obtained by graphical interpolation. It will be observed that  $r$  is always less than unity, i.e. that not all the added fertiliser phosphate remains in extractable form. In

TABLE III  
*Ratios of extractable to total fertiliser and soil phosphate*

Extraction Procedure Soil No.	Bray				Olsen				0.3 N HCl				Saunders				Dyer				
	In.	r	Equ.	P <sub>e</sub> /P <sub>t</sub>	In.	r	Equ.	P <sub>e</sub> /P <sub>t</sub>	In.	r	Equ.	P <sub>e</sub> /P <sub>t</sub>	In.	r	Equ.	P <sub>e</sub> /P <sub>t</sub>	In.	r	Equ.	P <sub>e</sub> /P <sub>t</sub>	
I	.95	.51	18	.21	.81	.45	18	.21	.86	.48	18	.12	.29	.65	30	.43	.89	.68	18	18	0
II	.81	.60	18	.22	.71	.44	10	.13	.66	.42	18	.13	.38	.68	25	.42	.81	.73	10	0.21	
III	.67	.37	18	.14	.56	.29	18	.09	.31	.18	18	.06	.80	.99	25	.33	.47	.37	18	0.09	
IV	.60	.23	18	.05	.59	.21	18	.02	.31	.12	8	.03	.72	.96	40	.18	.43	.22	10	0.04	
V	.56	.24	18	.12	.56	.20	10	.05	.20	.09	10	.03	.71	.95	40	.25	.33	.19	10	0.01	
VI	.42	.15	10	.01	.47	.16	15	.01	.08	.04	10	0	.70	.96	10	.17	.18	.08	10	0.01	
VII	.27	.13	10	.01	.39	.18	15	.02	.44	.02	15	0	.86	.96	10	.16	.08	.05	10	0.01	
VIII	.15	.08	8	.02	.22	.12	10	.03	.06	.03	7	.01	.95	.98	25	.24	.10	.07	10	0.01	

In. = Initial

Equ. = Equilibrium

r = ratio of extractable to total fertiliser phosphate (determined radiometrically).

P<sub>e</sub> = phosphate extractable by given method.P<sub>t</sub> = total soil phosphate determined by perchloric acid method.

the case of Saunder's method, however, almost all the fertiliser phosphate is extractable at equilibrium in six of the eight soils. It will be also seen that the initial values of  $r$ , obtained after only 4 h contact between soil and fertiliser, during air-drying, are in general considerably less than unity, implying that the added fertiliser phosphate undergoes extremely rapid transformation. There is good correlation between the initial and equilibrium values of  $r$  with all extraction procedures except that of Saunder; in the case of the latter there was apparently a reversal of the initial change. This is strikingly illustrated in Fig. 1, where typical results of the 0.3 N hydrochloric acid and Saunder's extraction procedures are plotted for soils numbered II and VI. The lines sketched through the plotted points clearly show the transformation and reversion indicated by the different methods.

Table III contains, for each soil, the ratios of extractable to total phosphate, calculated from the figures in Table I. It will be noted that the radiometric ratio,  $r$ , for the added fertiliser phosphate, does not at equilibrium attain the same value as the chemical ratio  $P_e/P_t$  for the soil,  $r$  is always greater than  $P_e/P_t$ .

#### DISCUSSION

The extractable fertiliser phosphate can be assumed to suffer dilution by the extractable soil phosphate and the total fertiliser phosphate can be assumed to undergo dilution by such soil phosphate as is present in labile form. According to the principles of isotopic dilution we can therefore define the labile phosphate content of the soil by the equation

$$r = \frac{P_e}{P_1},$$

where  $P_1$  is the labile soil phosphate in p.p.m.  $P_2O_5$ .

Since from our results,

$$r > \frac{P_e}{P_t},$$

it must be concluded that not all the soil phosphate is labile in the sense of the above definition.  $P_1$  has been calculated by the above equation for the soils considered here and the results are given in Table IV.

These results are derived from single, rather imprecise, colorimetric determinations of relatively small amounts of phosphate. Since the work was not duplicated the interaction of the first order, viz, that of method  $\times$  soil had to form the error term in an analysis of variance to provide a measure of the standard error. In this manner no difference can be detected between methods. It can therefore be said that  $P_1$ , on the average, is independent of the extraction procedure used. It is, however, dependent on the soil (the variance due to soil being significant at less than the 0.1% level) and must therefore be accepted as a characteristic soil property.

TABLE IV

Soil No.	I	II	III	IV	$\frac{P_1}{V}$	(p.p.m.) VI	VII	VIII
<b>Extraction Procedure</b>								
Bray	14	67	178	157	321	33	15	500
Olsen	16	52	148	76	165	38	28	392
0.3N Hydrochloric acid	8	57	144	150	244	0	0	467
Saunder	23	112	155	123	169	74	47	450
Dyer	0	52	108	118	47	38	40	371

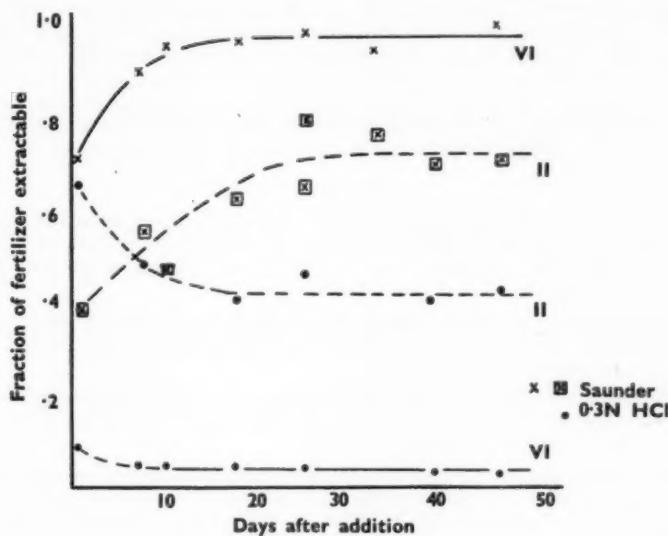


FIG. 1.

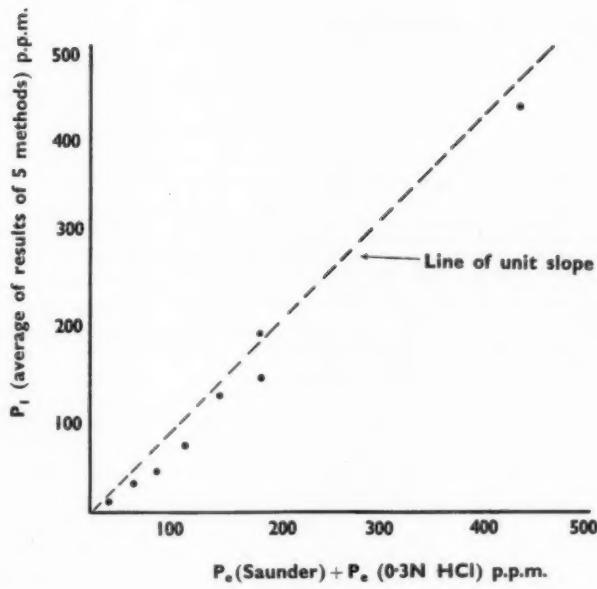


FIG. 2.

It will be observed (from Table III) that the sum of the *r* values for the Saunder and 0.3N hydrochloric acid extraction procedures approximates more closely to unity than does the sum of any other combination of procedures. This suggests that the labile phosphate can be measured by the sum of the Saunder and 0.3N hydrochloric acid extractable phosphate. The validity of this conclusion is graphically demonstrated in Fig. 2. It may be noted that in all but two of the soils the Saunder's method alone gives a good estimate of the labile phosphate.

#### CONCLUSION

1. The water soluble fertiliser phosphate is quickly distributed throughout the labile forms of soil phosphate and the fraction of fertiliser phosphate which remains available at equilibrium is equal to the fraction of the original labile soil phosphate which was available.

2. The labile phosphate in a soil can be measured as the sum of the Saunder and 0.3N hydrochloric acid extractable phosphates, or for some soils by the Saunder extractable phosphate alone.

3. The Saunder extraction does not measure soil phosphate which is available in the same sense as that determined by the methods of Bray, Olsen or Dyer, or by 0.3N hydrochloric acid extraction.

It may be pointed out that good results have been obtained<sup>10</sup> in crop yield prediction studies based on the findings reported here.

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#### REFERENCES

- 1 Williams, *Trans. Soc. Soil. Sci.*, 1951, **1**, 31.
- 2 Yuen and Pollard, *J. Sci. Fd. Agric.*, 1951, **2**, 186.
- 3 McAuliffe, Hall, Dean and Hendricks, *Proc. Soil. Soc. Amer.*, 1948, **12**, 119.
- 4 Talibudeen, *Radioisotope Conference*, 1954, **1**, 45.
- 5 Piper, *Soil and Plant Analysis*, University of Adelaide Press, 1944, p. 97.
- 6 Bray and Kurtz, *Soil Sci.*, 1945, **59**, 39.
- 7 Olsen, *U.S.D.A. Circular No. 939*, 1947.
- 8 Saunder, *Soil Sci.*, 1956, **82**, 456.
- 9 Dyer, *Trans. Chem. Soc.*, 1894, **65**, 115—as modified by A.E. & C.I. Research Department and Stellenbosch University for application to S.A. soils.
- 10 Mackenzie, Marr and Stiven, following paper.

## AN EQUATION FOR THE PREDICTION OF THE RESPONSE OF CROPS TO SUPERPHOSPHATE ON THE BASIS OF SOIL ANALYSIS

by

H. A. E. MACKENZIE, H. MARR and G. STIVEN

## OPSOMMING

'n Vergelyking, gelykvaarig aan dié van Mitscherlich (1909) om die relatiewe oesopbrengs volgens grondtelling en die hoeveelheid superfosfaat toegedien, te voorspel, is van 'n veronderstelde wet van afnemende wins afgelei. Daar is gevind dat die vergelyking 'n goeie kwantitatiewe weergawe is van die opbrengs tydens superfosfaat toediening op koring in twee distrikte van die Kaap Provincie gedurende 1955-56, en op mielies in Transvaal gedurende 1957, in beide gevalle met en sonder die toediening van stikstof.

## SUMMARY

An equation similar to that of Mitscherlich's (1909) for predicting relative crop yields in terms of the quantity of superphosphate applied and soil analyses only, is derived from an assumed law of diminishing returns. The equation has been found to give a good quantitative representation of the results of superphosphate response experiments carried out on wheat in two districts of the Cape Province during 1955-1957, with and without the application of nitrogen, and on maize in the Transvaal during 1957, with and without the application of nitrogen.

One of the central problems of agricultural chemistry is to discover the relationship between the chemical composition of soils and the yield which can be harvested from crops grown on such soils. Furthermore, the application of fertiliser to a soil will, in general, change both the composition of the soil and the crop yield which that soil will bear. The prediction of these effects is of considerable economic importance. The technique of linear correlation has for many years been used to relate soil "status", as measured by empirical chemical procedures, to crop yield and fertiliser response, but the technique has yielded no quantitative generalisations because the correlations have been found to vary from season to season, from soil type to soil type and from crop to crop.

The work reported here is an attempt to approach the problem along fundamental lines and to establish a functional relationship between soil "status", crop yield and fertiliser application; it is preliminary in character and the conclusions can be established only by prolonged and continued testing against experimental results.

## DERIVATION OF PREDICTION EQUATION

It has long been known<sup>1</sup> and can be accepted as axiomatic that the response of a crop to fertiliser application follows a law of diminishing returns. Mitscherlich<sup>2</sup> has formulated this law by setting the rate of increase of crop yield with fertiliser application proportional to the decrement of the yield from the asymptotic limit which it approaches as the fertiliser application is indefinitely increased. Numerous other authors have used his equation or adapted it by modification in definition.

We assume that the law takes the form:

where  $y$  is the yield of crop per acre obtained when a specified nutrient is at activity  $n$  in the soil,  $A$  is the value which  $y$  approaches asymptotically as  $n$  is increased and

$c$  is a factor of proportionality (akin to Mitscherlich's "Wirkungsfaktor").  $A$  is, of course, dependent upon all those factors, other than the specified nutrient, which influence yield and is constant only if these factors are maintained constant. Integration of equation (1), assuming that zero nutrient activity implies zero yield, gives

The activity,  $n$ , of a nutrient in the soil is made up of two contributions, one from nutrient native in the soil and one from nutrient added in the form of fertiliser.

i.e.  $n = n_0 + n_a$ , ... (3)

where  $n_0$  is the activity of the native nutrient and  $n_a$  is the increase in nutrient activity which results from fertiliser addition. Hence

$$v/A = 1 - e^{-c(n_o + n_a)} \quad \text{at } v = 0 \quad (4)$$

The problem now is to determine what chemical or other measures can be used for  $n_0$  and  $n_a$ . In the case where the applied fertiliser is superphosphate we have adopted the following hypotheses:

1. We have assumed that  $n_0$  is identical with the concentration of plant-available  $P_2O_5$  in the soil, written as  $P_A$ . (Numerous chemical extraction procedures have been devised to give results which can be regarded as estimates, some good, some bad, of  $P_A$ . A choice among these procedures for determining extractable  $P_2O_5$  must ultimately be made on the basis of comparison with crop response.) If  $P_A$  is expressed in p.p.m., we can write

$$n_0 = k \cdot P_A \text{ lb/acre} \quad \dots \quad (5)$$

where  $k$  is simply a factor which converts from units of p.p.m. of nutrient in the soil to lb nutrient per acre; this depends on soil density over the depth of soil used for the estimation of  $P_A$ .

2. We have assumed that water-soluble  $P_2O_5$ , when applied to soil, rapidly undergoes change so as to conform to the soil pattern of  $P_2O_5$ . It is well-known<sup>3</sup> that not all added  $P_2O_5$  is available to a crop during one season; furthermore, it has been shown<sup>4</sup>, by isotopic studies on selected but widely different soil types, that the fraction of applied water-soluble  $P_2O_5$  which survives in an extractable form is equal to the fraction of the labile native  $P_2O_5$  which was extractable. Our assumption is thus substantiated by known facts.

Accordingly, if superphosphate is applied at a rate equivalent to  $x$  lb  $P_2O_5$ /acre, we write

where  $P_L$  is the labile soil  $P_2O_5$  in p.p.m.

The adoption of these two assumptions enables us to re-write equation (4) as:

which is our fundamental prediction equation. It should be noted that the product  $c.P_A$  appears in the equation. A great deal of controversy<sup>5</sup> arose over Mitscherlich's claim for the constancy of his effect factor and still continues<sup>6, 7, 8</sup> in more recent literature. In our view the polemics have been largely at cross purposes because our equation reveals that apparent variations in  $c$  can result merely from variation in the goodness of estimates of  $P_A$  made by chemical extraction or other procedures; in principle a chemical method for estimating  $P_A$  could be chosen on the criterion of the constancy of  $c$ .

For zero fertiliser application, equation (7) becomes

and hence the yield with applied fertiliser relative to that with no fertilizer application is

If a suitable choice can be made of analytical methods for the estimation of  $P_A$  and  $P_L$  and of values for the constants  $c$  and  $k$ , the equation provides a means for calculating, from soil analysis only, the increase in crop yield which can be expected from a given fertilizer application.

## APPLICATION OF THE PREDICTION EQUATION

The application of equation (9) rests on the estimation of  $P_A$ ,  $P_L$  and the two constants  $c$  and  $k$ .  $P_A$ , which is the plant-available  $P_2O_5$  in a soil, is, in principle, correctly determined by plant response studies and  $P_L$  by work of the type described by Rijkheer<sup>4</sup>.

It would, however, be convenient if chemical methods could be selected, from those available in the literature, for the analytical estimation of  $P_A$  and  $P_L$ . With this object in view we have carried out a great deal of computational work that need not be elaborated here. The solution of simultaneous equations of the form (7) using yields obtained in the field for different fertiliser treatments has been used to provide values of  $P_A$ , and for this purpose an electronic analogue computer was designed and constructed by Aarts<sup>9</sup>. Correlation between the agronomically derived values of  $P_A$  and chemically extractable  $P_2O_5$  has shown that several chemical procedures, including those of Dyer<sup>10</sup> and Bray<sup>11</sup> and a 0.3 N hydrochloric acid extraction, give good estimates of  $P_A$ . The work of Rijkheer (*loc. cit.*) has shown that  $P_L$  is well correlated with the sum of 0.3 N HCl-extractable  $P_2O_5$  and alkali-extractable  $P_2O_5$  (Saunders<sup>12</sup>) and that even the latter alone gives a good estimate of  $P_L$ .

In the tests of our prediction equation reported in this paper we have used Dyer-, Bray- or 0.3 N HCl-extractable  $P_2O_5$  to estimate  $P_A$  and Saunder-extractable  $P_2O_5$  to estimate  $P_L$ .

We have assigned to the constant  $c$  a value of 0.016 acre/lb  $P_2O_5$ , a weighted mean of the values used for the Mitscherlich effect factor by Mitscherlich<sup>13</sup>, Crowther and Yates<sup>14</sup> and van der Paauw<sup>8</sup>. The constant  $k$  has been given a value of 2 lb/acre per p.p.m. on the basis of the agronomic rule-of-thumb that an acre of soil to a depth of 6 ins weighs  $2 \cdot 10^6$  lb; the value is not unreasonable in the light of Goldschmidt's work<sup>15</sup>.

The easiest way to use the equation is by means of nomograms, an example of which is shown in Fig. 1. This shows the percentage increase in yield that can be expected on soils having certain values of  $P_A$  and  $P_L$  when superphosphate is applied at 100 lb  $P_2O_5$ /acre.

## TEST OF PREDICTION EQUATION

The experimental field data available to us for testing the prediction equation consisted of the result of experiments conducted by our colleagues on wheat in Ruens and Swartland during 1955 and 1956 and on maize in the Transvaal highveld during the 1956/1957 summer; in some of the experiments nitrogen was applied as an additional treatment. The data are recorded in the accompanying Tables I, II and III.

together with the observed yields and the yields calculated by our prediction equation. These represent all data that could be tested by our equation. Such other agronomic data as exist cannot be used for testing because soil analyses do not accompany field yields.

The calculated yields for the Bray method of extraction are plotted against the observed yields in Fig. 2. The line of unit slope in the figure is the line upon which points would fall in cases of exact agreement between calculated and observed yields. Points falling on the dotted lines in the figure represent cases in which the calculated and observed yields disagree by 20 per cent. of the value of the observed results. The figure shows that 70 per cent. of the calculated yields agree, to within 20 per cent.,

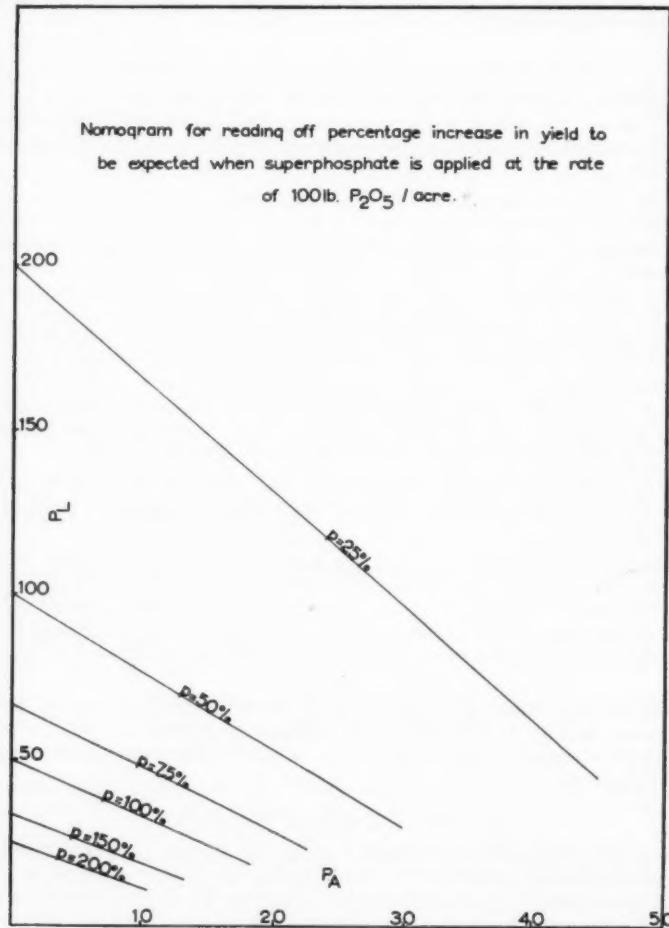


FIG. 1

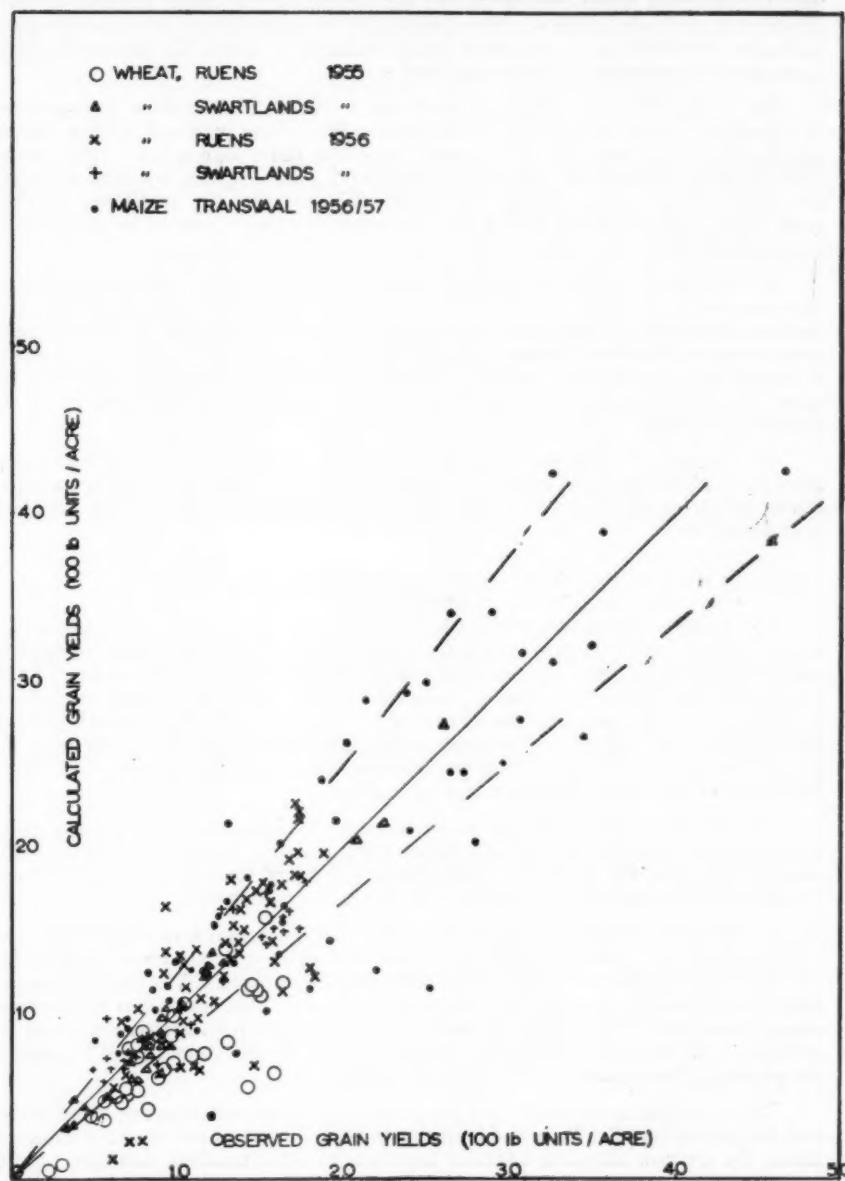


FIG. 2

with the observed yields. Similar figures were drawn for the Dyer- and 0.3N hydrochloric acid methods and it was found impossible to judge by eye which of the three extraction methods gave calculated yields which best fitted the observed yields. Consequently statistical tests were applied.

For each of the three extraction methods, a statistical analysis of the regression of calculated yields on observed yields gives a line whose intercept does not differ significantly from zero and whose slope does not differ significantly from unity. Since the ideal relationship between calculated and observed yields would be a straight line of unit slope passing through the origin, it is seen that the prediction equation gives results which are not biased and this absence of bias persists for all levels of predicted yields.

To find which method of extraction gives the closest fit of calculated yields to observed yields, the variances of deviations of the plotted points from their respective regression lines were calculated for the three extraction methods. A variance ratio comparison of the three variances showed the 0.3N hydrochloric acid extraction to be significantly (at the .05 level of significance) poorer for predicting yields than the other two methods. The Dyer and Bray methods could not be distinguished by the variance-ratio test.

The variance of differences between observed and calculated yields was calculated for each of the three extraction methods and a comparison of these variances confirmed the superiority of the Dyer and Bray methods over the 0.3N hydrochloric acid extraction.

#### DISCUSSION

The prediction equation derived here has already been shown to possess a high degree of generality, but its accuracy and utility must be tested by continued application. We have been able to predict crop yield increases under a wide variety of field conditions, and furthermore these predicted increases have been made completely independent of any precognition of soil type, climatic conditions, variety of crop, season of the year, age of the land or its cropping history, or any other criteria except the results of chemical soil tests, the quantity of superphosphate applied, and a knowledge of the yield before fertilizer application.

The effects of changes in the magnitudes of the parameters in equation (9) on the calculated yields have been calculated. Differentiating the equation in turn with respect to  $y_0$ ,  $P_A$ ,  $P_L$ ,  $x$ ,  $k$  and  $c$ , formulae are obtained for relative changes in predicted yields corresponding to relative changes in the parameters.

In Table IV are given the percentage errors in the parameters required to cause a 1% error in the predicted yield. The effect of error in  $y_0$  is not given in the table, since it is obvious that a 1% error in  $y_0$  will give a 1% error in  $y$ . The prediction equation is most sensitive to errors in  $y_0$  and  $k$  in that order. This means that the accuracy of any prediction rests largely on the precision with which  $y_0$  is measured, and the accuracy with which  $k$  is estimated, whilst errors in the determination of  $P_A$  and  $P_L$  do not effect the calculated yield quite so seriously.

The assumption on which our prediction equations rest appears to be sound, and the parameters  $P_A$ ,  $P_L$ ,  $c$  and  $k$  appear to be well represented by our estimates of them. We are now adopting a similar approach to other nutrient elements, notably potash and nitrogen. In regard to the latter a large number of field experiments are at present in progress in conjunction with intensive laboratory studies.

TABLE I

Districts: Swartlands and Ruens, C.P. Crop: Winter Wheat. Year: 1955  
 Fertiliser Application: 0, 50, 100 lb  $P_2O_5$ /acre, applied as superphosphate  
 $y_0$ ,  $y_1$  and  $y_2$  are the corresponding yields

Experimental Site No.	Estimate of Available $P_2O_5$ (p.p.m.)			Observed Grain Yields 100 lb units/acre			Calculated Grain Yields 100 lb units/acre								
	NH <sub>4</sub> F & HCl (Bray 11)	Citric Acid (Dyer 10)	0.3N HCl	Y <sub>0</sub>			Y <sub>1</sub>			Y <sub>2</sub>			Y <sub>1</sub>		
				Y <sub>0</sub>	Y <sub>1</sub>	Y <sub>2</sub>	Y <sub>1</sub>	Y <sub>2</sub>	Y <sub>3</sub>	Y <sub>1</sub>	Y <sub>2</sub>	Y <sub>3</sub>	Y <sub>1</sub>	Y <sub>2</sub>	Y <sub>3</sub>
Swart-lands	32	31	20	15	140	6.80	8.44	9.53	7.45	8.00	7.62	8.35	7.71	8.54	8.54
	2	33	24	18	5.17	6.26	7.08	5.64	6.04	5.74	6.24	5.82	6.40	6.40	6.40
	31	45	34	18	170	3.27	3.26	3.53	3.03	3.17	3.07	3.26	3.16	3.43	3.43
	27	53	35	28	180	7.62	8.98	8.98	7.98	8.26	8.16	8.61	8.24	8.78	8.78
	4	20	29	12	120	7.76	8.98	8.98	8.84	9.79	9.38	9.04	10.21	10.21	10.21
	15	35	34	19	160	9.44	9.89	10.35	10.18	10.19	10.83	10.46	11.39	11.39	11.39
	37	91	80	61	220	4.22	4.36	4.41	4.29	4.34	4.31	4.38	4.36	4.47	4.47
	19	76	55	45	250	6.81	7.21	6.95	7.06	7.04	7.23	7.09	7.34	7.34	7.34
	3	56	43	31	160	7.78	8.16	8.18	8.46	8.36	8.82	8.44	9.00	9.00	9.00
	20	66	52	34	160	4.63	3.81	5.72	4.81	4.94	4.88	5.07	4.93	5.24	5.24
	21	52	35	24	170	11.57	11.84	12.16	12.61	12.42	13.14	12.63	13.59	13.59	13.59
	22	31	18	18	140	5.44	8.98	5.96	6.40	6.12	6.74	6.74	6.74	6.74	6.74
	10	48	37	37	120	18.92	20.69	22.32	20.34	21.37	20.75	22.17	22.17	22.17	22.17
	25	83	48	48	160	9.53	10.07	10.21	9.77	9.94	10.08	10.53	10.08	10.53	10.53
	28	68	60	34	170	8.03	8.17	8.31	8.52	8.37	8.62	8.63	9.15	9.15	9.15
	17	50	53	35	160	12.38	12.80	12.12	13.07	13.61	13.03	13.34	14.15	14.15	14.15
	30	116	112	83	180	10.21	9.26	9.39	10.32	10.37	11.14	11.22	10.45	10.61	10.61
	12	58	68	44	150	25.18	—	26.00	26.42	27.33	26.16	26.84	26.88	26.88	26.88
Ruens	23	2	7	1	14	0.14	2.18	3.13	0.47	0.72	0.32	0.48	0.47	0.78	0.78
	14	19	12	9	90	4.67	14.16	15.79	5.54	6.27	5.68	6.59	5.75	6.74	6.74
	9	17	12	8	110	3.13	5.58	8.17	3.63	4.08	3.69	4.20	3.74	4.31	4.31
	26	38	22	14	150	7.08	11.57	13.07	7.63	8.07	7.85	8.53	7.98	8.82	8.82
	24	15	17	7	80	3.83	5.61	6.89	4.69	5.44	4.66	5.35	4.86	5.82	5.82
	6	35	27	26	90	5.36	8.80	9.18	6.05	6.56	6.19	6.85	6.21	6.89	6.89
	35	37	17	17	160	4.63	6.26	7.63	4.98	5.26	4.98	5.26	5.15	5.63	5.63
	18	38	35	20	180	4.08	5.72	6.56	4.35	4.57	4.37	4.62	4.47	4.82	4.82
	33	26	21	11	160	10.07	15.11	16.34	11.02	11.85	11.12	12.06	11.36	12.57	12.57
	1	41	30	26	200	6.67	9.80	10.75	7.04	7.36	7.14	7.55	7.18	7.64	7.64
	41	59	40	34	160	4.59	6.12	6.89	4.80	4.96	4.91	5.17	4.95	5.26	5.26
	11	39	36	16	190	3.54	4.76	5.03	3.76	3.94	3.77	3.97	3.88	4.21	4.21
	38	76	50	61	200	10.96	—	14.28	11.24	11.44	11.46	11.87	11.35	11.66	11.66
	5	70	50	48	260	11.16	12.66	14.43	11.42	11.62	11.56	11.91	11.52	11.94	11.94
	13	25	20	9	160	6.13	7.35	7.63	6.71	7.24	6.78	7.37	6.94	7.71	7.71
	36	19	21	9	90	1.71	—	15.24	13.88	15.72	13.79	15.51	14.41	16.90	16.90
	8	45	41	29	240	7.62	8.44	7.95	8.23	8.23	8.28	8.17	8.17	8.65	8.65
	29	66	54	38	200	9.26	9.53	9.66	9.53	9.76	9.62	9.91	9.76	10.20	10.20
	7	50	30	200	12.80	—	12.80	13.39	13.87	13.34	13.77	13.70	14.50	14.50	14.50
	16	41	27	22	220	7.21	6.67	7.08	7.57	7.90	7.83	8.15	7.75	8.25	8.25
	34	55	35	35	150	8.17	9.25	7.76	8.60	8.92	8.94	9.59	8.84	9.40	9.40

Soil types  
 C.R.  
 v.d. Merwe

Gravelly  
 Sandy  
 Loams on  
 Clay  
 Rainfall  
 generally  
 much  
 lower in  
 this dis-  
 trict than  
 in Ruens.  
 It ranges  
 from 12-  
 16 in to  
 16-20 in  
 annually.

TABLE II

Districts: Swartlands and Ruens, C.P. Crop: Winter Wheat. Year: 1956

Nitrogen was applied as Ammonium Nitrate  
Fertilizer application: 0 lb N/acre } Without  $P_2O_5 = y_0$   
10 " " } With  $100 \text{ lb } P_2O_5/\text{acre} = y_1$   
20 " " }  
" " " }  
" " " }

Experimental Site No. Swart- lands	Estimate of available $P_2O_5$ (p.p.m.)		Estimate of labile $P_2O_5$ (p.p.m.) (NaOH <sup>12</sup> )	$y_0$	$y_1$	Calculated grain yields 100 lb units/acre			Soil types after C.R. v.d. Merwe
	NH <sub>4</sub> F + HCl (Bray <sup>1</sup> )	Citric Acid (Dyer <sup>10</sup> )				Bray $y_1$	Dyer $y_1$	0-3 N HCl $y_1$	
110	28.5	34.0	7.5	167	5.70	8.88	6.68	6.45	7.16
					7.37	9.38	8.63	8.34	9.25
					8.21	5.86	9.62	9.29	10.31
227	61.2	54.0	21.8	158	13.97	17.42	15.03	15.13	16.71
					16.52	17.79	17.77	17.89	19.76
					17.91	18.86	19.27	19.45	21.49
150	110.3	84.0	36.3	223	6.53	6.23	5.11	5.28	5.67
					6.84	6.83	6.64	6.62	7.21
					6.26	5.63	6.95	7.04	7.55
194	40.7	38.5	10.5	188	5.93	6.00	5.83	5.82	6.39
					6.00	6.58	6.56	7.20	
248	65.1	37.7	11.4	276	6.90	7.07	7.64	8.38	
					6.94	7.37	7.25	7.48	7.95
					7.61	8.04	7.95	8.20	8.72
224	100.8	94.3	30.3	229	9.82	10.29	10.26	10.58	11.25
					12.90	13.23	13.16	13.18	15.13
					14.24	15.08	14.53	14.55	16.70
					15.41	16.42	15.73	15.74	18.08
242	73.3	56.5	20.4	179	6.20	5.03	6.51	6.59	7.32
					6.87	5.70	7.22	7.30	8.12
					7.20	6.70	7.57	7.64	8.51
218	100.2	88.7	35.1	233	15.75	12.73	16.08	16.14	17.37
					15.75	13.40	16.08	16.14	
					16.75	15.25	17.10	17.17	18.48
73	95.0	88.6	40.8	60	11.39	16.52	11.50	11.95	14.19
					15.85	16.75	16.01	16.64	19.75
					14.98	15.85	15.13	15.72	18.67
61	81.0	58.9	38.6	140	11.39	12.73	11.94	12.30	13.06
					13.40	15.41	14.06	14.47	15.36
					14.07	16.42	14.76	15.19	16.24
104	96.4	92.5	44.5	96	10.12	10.51	10.50	11.82	
					—	—	—	—	—
					8.88	11.83	9.21	9.21	10.37

TABLE II—(continued)

Experimental Site No. Rueens	Estimate of available $P_2O_5$ (p.p.m.)			Estimate of labile $P_2O_5$ (p.p.m.) NaOH (Saunders <sup>12</sup> )	Observed grain yields 100 lb units/acre	Calculated grain yields 100 lb units/acre			Soil types after C.R. v.d. Merwe
	$NH_4^+ F +$ HCl (Bray <sup>11</sup> )	Citric Acid (Dyer <sup>10</sup> )	0.3 N HCl			Y <sub>0</sub>	Y <sub>1</sub>	Bray Y <sub>1</sub>	
29	41.6	44.9	14.9	90	12.60	14.14	14.97	14.98	17.40
				14.61	14.78	17.35	17.37	20.17	
129	44.6	33.9	16.7	192	15.08	15.25	17.91	17.92	20.82
				11.83	13.17	12.99	13.21	14.00	
79	79.3	59.6	23.1	242	12.50	13.84	13.73	13.96	14.80
				12.97	12.73	14.24	14.49	15.35	
				10.22	11.23	10.58	10.75	11.54	
				—	—	—	—	—	
163	30.0	30.3	7.3	108	11.56	12.90	11.97	12.16	13.06
				12.30	13.64	15.04	14.85	17.08	
37	79.2	60.3	27.2	183	14.74	15.18	16.92	16.70	19.22
				14.74	15.18	18.03	17.79	20.47	
98	46.0	44.2	12.8	243	8.11	8.38	8.45	8.62	9.35
				8.38	—	8.45	8.91	9.66	
49	53.7	41.3	14.3	185	10.05	10.62	10.48	10.69	11.58
				10.05	10.62	8.31	8.29	8.94	
212	137.4	128.9	2.6	331	7.71	7.87	8.48	8.46	9.13
				7.87	7.71	9.39	9.36	10.10	
206	31.8	24.3	5.4	162	15.41	15.58	16.66	16.92	18.49
				17.76	16.92	19.20	19.50	21.32	
123	25.2	22.9	4.2	112	18.09	17.26	19.56	19.86	21.71
				17.59	16.42	17.69	17.70	20.15	
				18.09	17.26	18.20	18.20	20.72	
				19.27	18.93	19.38	12.39	22.07	
				19.10	17.42	22.01	22.36	24.36	
				18.93	17.26	21.82	22.16	24.14	
				19.27	17.09	22.21	22.56	24.58	
				1.04	6.30	1.29	1.29	1.46	
				1.68	7.14	2.09	2.09	2.36	
				1.88	7.97	2.34	2.34	2.64	
				5.19	11.56	6.56	7.38	7.24	
				5.36	14.58	6.79	7.63	7.48	
				4.19	13.40	5.31	5.96	5.85	

TABLE II—(continued)

Experimental Site No. Ruens	Estimate of available $P_2O_5$ (p.p.m.)			Estimate of labile $P_2O_5$ (p.p.m.) NaOH (Saunders <sup>12</sup> )			Observed grain yields 100 lb units/acre			Calculated grain yields 100 lb units/acre.			Soil types after C.R. v.d. Merwe
	NH <sub>4</sub> F + HCl (Bray <sup>11</sup> )	Citric Acid (Dyer <sup>10</sup> )	0.3 N HCl	y <sub>0</sub>	y <sub>1</sub>	Bray y <sub>1</sub>	Dyer y <sub>1</sub>	0.3 N HCl y <sub>1</sub>	Bray y <sub>1</sub>	Dyer y <sub>1</sub>	0.3 N HCl y <sub>1</sub>		
14	23.0	19.2	3.8	150	11.06	15.85	13.02	13.32	14.45	12.87	13.96		
8	32.3	24.9	7.9	137	10.69	17.99	12.59	12.22	13.26	11.95	13.26		
182	31.4	30.9	8.3	134	8.21	18.19	11.95	12.22	10.72	9.81	10.65		
133	76.4	50.8	28.3	236	9.08	11.36	9.63	9.81	11.86	10.65	10.85		
85	20.7	16.1	5.6	242	9.25	12.23	10.85	11.05	12.09	10.25	10.85		
188	15.9	14.0	4.7	80	7.37	10.22	8.70	8.64	9.65	8.04	8.70		
157	32.4	23.2	9.3	87	5.36	7.71	8.88	8.00	8.62	6.09	6.11		
43	67.8	62.6	24.2	100	5.70	7.04	6.48	6.50	6.35	5.72	6.48		
200	51.2	36.7	14.4	150	6.03	11.06	6.85	6.87	7.15	11.48	11.95		
67	62.8	63.1	13.0	92	6.03	13.40	15.36	15.35	16.93	15.36	15.35		
117	32.9	32.2	8.4	153	6.70	10.89	13.23	15.36	16.93	11.39	11.95		
33	59.9	45.4	15.4	190	7.71	9.38	7.71	10.19	11.70	10.61	11.70		

TABLE III  
*Districts: Maize Triangle, Transvaal. Crop: Summer Maize. Year: 1956/57*  
*Nitrogen was applied in the form of Urea*

Experimental Site No.	Estimate of available $P_4O_6$ (p.p.m.)			Observed grain yields 100 lb units/acre			Calculated grain yields 100 lb units/acre			Soil types	
	NH <sub>4</sub> F + HCl (Bray <sup>11</sup> )	Citric Acid (Dyer <sup>10</sup> )	0.3 N HCl	$y_0$	$y_1$	$y_2$	Bray $y_1$	Dyer $y_1$	0.3 N HCl $y_1$		
1	19.8	36.2	22.4	102.0	17.9	12.88	11.95	12.73	8.0	Black Turf.	
2	3.24	13.8	6.0	110.0	27.7	21.4	26.95	28.33	3.8	<sup>12</sup>	
3	44.5	20.0	9.6	239.0	11.5	12.3	14.75	15.38	17.78	Rred Sandy Loam.	
4	30.4	12.2	9.2	135.0	29.0	32.6	31.06	32.47	33.30	<sup>12</sup>	
5	81.2	41.3	32.5	168.0	10.0	9.5	11.60	12.41	12.58	13.0	
6	27.9	10.5	3.1	130.0	49.6	24.0	20.99	21.95	22.50	<sup>12</sup>	
7	75.5	32.8	28.7	200.0	15.8	16.6	16.42	17.50	17.66	7.5	
8	37.9	17.1	8.9	91.0	14.6	15.6	15.18	16.17	16.32	<sup>12</sup>	
9	19.7	11.4	0.73	116.0	3.2	12.1	3.79	4.19	4.41	7.5	
10	31.8	19.1	8.15	106.5	6.4	6.4	7.57	8.38	8.81	<sup>12</sup>	
11	10.2	9.4	0.0	93.5	116.0	9.8	13.0	12.10	12.59	13.42	11.0
12	157.0	113.5	89.1	245.0	16.4	16.2	20.25	21.07	22.46	Red Loam.	
13	46.0	24.9	17.6	122.5	7.1	5.1	8.44	8.92	9.45	<sup>12</sup>	
14	27.8	15.0	5.4	114.0	7.2	9.6	8.56	9.05	9.58	<sup>12</sup>	
15	34.4	17.1	8.7	118.5	7.9	15.4	10.00	10.78	—	14.5	
16	24.0	15.1	3.8	124.5	10.4	15.7	17.72	19.10	—	<sup>12</sup>	
17	28.3	18.1	64.2	155.0	245.0	20.3	27.8	20.56	20.79	20.0	<sup>12</sup>

TABLE III—(continued)

Exper- imental Site No.	Estimate of available $P_2O_5$ (p.p.m.)		Estimate of labile $P_2O_5$ (p.p.m.) (Saunders <sup>12</sup> )	Observed grain yields 100 lb units/acre		Calculated grain yields 100 lb units/acre		Plant population (1,000 s) acre	Soil types
	NH <sub>4</sub> F + HCl (Bray <sup>13</sup> )	0.3 N HCl (Dyer <sup>14</sup> )		$y_6$	$y_1$	Bray $y_1$	Dyer $y_1$		
18	21.6	18.6	5.7	165.5	18.6	19.6	21.63	21.84	Inter-zonal Brown loam.
19	66.1	53.6	31.3	130.5	22.6	20.2	26.29	26.53	7.43
20	42.8	29.4	14.7	148.0	6.4	6.4	6.84	7.00	15.3
21	13.2	10.6	2.1	124.0	13.6	19.2	14.32	14.88	15.80
22	85.2	55.1	60.2	107.0	17.0	14.8	13.11	13.59	14.28
23	43.9	23.9	11.9	111.0	21.0	15.4	17.33	17.96	15.0
24	34.6	27.3	17.2	93.0	9.6	13.0	21.36	21.62	12.5
25	34.9	30.7	16.4	74.5	19.1	18.7	23.99	24.29	25.36
26	30.3	27.4	10.7	65.0	23.3	27.2	24.38	25.73	25.42
27	33.4	29.7	15.4	70.2	30.2	30.9	31.60	33.35	33.06
28	31.2	261.0	237.0	390.0	10.1	10.9	12.60	13.55	14.34
29	34.6	16.7	9.1	118.5	12.3	12.3	12.96	15.02	9.4
30	28.9	26.6	13.2	49.5	8.7	9.7	10.71	11.41	11.5
31	21.6	25.2	8.6	77.0	8.2	8.8	10.24	10.46	7.5
					7.4	7.1	9.24	9.44	11.52
					15.8	12.5	15.80	15.80	11.40
					11.4	25.2	11.40	11.40	12.0
					29.3	26.5	34.04	36.53	47.32
					36.6	32.6	42.52	45.63	10.42
					6.6	6.7	8.87	9.14	12.0
					7.2	7.3	9.68	9.98	11.37
					25.8	29.0	34.00	33.26	37.29
					24.4	—	32.16	31.45	35.27

TABLE IV  
Percentage errors in parameters which will give 1% error in the calculation of  $y$

Values of			Errors		
x	PL	PA	PA or c	PL or x	k
50	50	12.5	12.0	4.1	3.1
		25.0	7.4	5.8	3.3
	100	25.0	14.1	8.6	5.3
		50.0	10.9	16.0	6.5
	200	50.0	20.7	25.3	11.4
		100.0	28.7	89.0	21.7
100	50	12.5	6.2	3.1	2.1
		25.0	4.0	4.9	2.2
	100	25.0	7.4	5.8	3.3
		50.0	6.1	12.5	4.1
	200	50.0	10.9	16.0	6.5
		100.0	16.3	67.0	13.1

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#### REFERENCES

- 1 Mill, *Principles of Political Economy*, George Routledge & Sons, Ltd., London, 1891, p. 129.
- 2 Mitscherlich, *Landw. Jahrb.*, 1909, **38**, 537.
- 3 Bear and Toth, *Ind. and Eng. Chem.*, 1942, **34**, 49.
- 4 Rijkheer, preceding paper.
- 5 Stewart, *Imp. Bureau of Soil Sci. Tech. Bull.*, No. 25, 1932.
- 6 Black & Kempthorn, *Agron. J.*, 1954, **46**, 303.
- 7 Bray, *Soil Sci.*, 1954, **78**, 9.
- 8 van der Paauw, *Plant and Soil*, 1952, **4**, 97.
- 9 Aarts, *S. Afr. J. of Sci.*, (In the Press).
- 10 Dyer, *J. Chem. Soc. (Trans.)*, 1894, **65**, 115.
- 11 Bray and Kurtz, *Soil Sci.*, 1945, **59**, 39.
- 12 Saunder, *Soil Sci.*, 1956, **82**, 457.
- 13 Mitscherlich, *Pflanzenernähr. Dungung. Bodenk.*, 1947, **38**, 22.
- 14 Crowther and Yates, *Empire J. of Exp. Agric.*, 1941, **9**, 77.
- 15 Goldschmidt, *S. Afr. J. of Sci.*, 1949, **45**, 88.

## NOTES

**THE DETERMINATION OF THE HALF-LIVES AND ALPHA-PARTICLE  
ENERGIES OF SOME RADIOACTIVE ISOTOPES**  
**PART III. THE ALPHA-PARTICLE ENERGY OF  $U^{233}$**

by

**F. L. CLARK, H. J. SPENCER-PALMER and R. N. WOODWARD**

We wish to draw attention to a measurement made by us which we believe was the first determination of the energy of alpha-particles of  $U^{233}$ . This was published as a British Atomic Energy Report<sup>1</sup> dated 27th June, 1945, which has just been declassified. The determination was carried out using an ionisation chamber and pulse analyser designed by O. R. Frisch<sup>2, 4</sup> and a method devised by us<sup>3, 5</sup> for the determination of alpha-particle energies with reference to those of  $Po^{210}$  (assumed to be 5.298 MeV).

A sample of  $U^{233}$  from Montreal was supplied by N. Feather in the form of the hydroxide of  $U^{233}$  containing about 15% of the hydroxide of  $U^{238}$ . This was converted into oxide and about  $8 \times 10^{-6}$  mg in nitric acid was evaporated to dryness, dissolved in 0.2 ml Zapon lacquer-acetic acid mixture and placed on platinum foil so as to occupy an area of 7 sq. cm. The deposit was dried, ignited, placed in an ionisation chamber filled with argon at atmospheric pressure and covered by a zinc collimator; the chamber used was such that alpha-particles of energy less than 5.7 MeV could not reach the grid.

The alpha-ray spectrum was scanned between 2.58 MeV and 6.03 MeV, and only one group was observed (the activity of the  $U^{238}$  being of course much too low to be detected). The mean of six separate determinations with reference to alpha-particles from  $Po^{210}$  gave a value of  $4.812 \pm 0.015$  Mev. The "spread" of the peak was not significantly different from that of the  $Po^{210}$  peak so that there was no evidence of any fine structure of alpha-particles.

This value of the alpha-particle energy has been confirmed by later workers, e.g.:—

1947 Chamberlain <i>et al</i> <sup>6</sup>	4.80 MeV
1947 English <i>et al</i> <sup>7</sup>	4.80 MeV
1948 Cranshaw <i>et al</i> <sup>8</sup>	4.823 MeV

It has more recently been showed by Asaro & Perlman<sup>9</sup> that a fine structure does exist, 15% of the alpha-particles being at 44 Kev and 2% at 94 Kev above the ground state, and this is confirmed by recent observations of gamma transitions by various workers.

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## REFERENCES

- 1 Clark, Spencer-Palmer and Woodward, *British Declassified Report BR159*, June, 1945.
- 2 Clark, Spencer-Palmer and Woodward, *British Declassified Report BR431*, May, 1944.
- 3 Clark, Spencer-Palmer and Woodward, *British Declassified Report BR522*, October, 1944.
- 4 Clark, Spencer-Palmer and Woodward, *J. S. Afr. Chem. Inst.*, 1957, **10**, 62.
- 5 Clark, Spencer-Palmer and Woodward, *J. S. Afr. Chem. Inst.*, 1957, **10**, 74.
- 6 Chamberlain, Gofman and Legre, *Phys. Rev.* 1947, **71**, 529.
- 7 English, Cranshaw, Demers, Harvey, Hinks, Jelley and May, *Phys. Rev.*, 1947, **72**, 253.
- 8 Cranshaw and Harvey, *Can. J. Research* 1948, **26A**, 243.
- 9 Hollander, Perlman and Seaborg, *Phys. Rev.*, 1953, **25**, 605.

## THE DETERMINATION OF ARSENIOUS OXIDE BY X-RAY DIFFRACTION ANALYSIS

by

J. W. MENARY

### OPSOMMING

'n Metode vir die bepaling van arseenoksied met behulp van X-straalanalise word beskryf. Die metode onderskei tussen arseenoksied en verbindings wat arseenoksied vrystel by behandeling met water.

### SUMMARY

A method for determining arsenious oxide by X-ray diffraction analysis is described. The method distinguishes between arsenious oxide and compounds which liberate arsenious oxide when treated with water.

### INTRODUCTION

While investigating mixtures containing arsenical compounds and sulphur it was found that classical methods of analysis did not distinguish adequately between the different forms in which the arsenic was combined. The mixtures being investigated had the following approximate composition: 23.5% arsenic (as  $As_2O_3$ ), 70.5% sulphur and 5.1% sodium (as  $Na_2O$ ). The arsenic was combined in the trivalent and pentavalent forms as oxides, sulphides and sulphur-arsenic complexes. A large proportion of the sulphur was present in the elemental state.

### EXPERIMENTAL

Sulphur was removed from the mixture by Soxhlet-extraction with carbon disulphide. The X-ray diffraction pattern of the residue, obtained with a Berthold recording diffractometer, showed that it was possible to determine arsenious oxide using zinc oxide as an internal standard. The standard gives three strong diffraction lines which do not interfere with lines from arsenious oxide or from other compounds present in the mixture. The method is of general applicability.

The material was crushed to pass a 325 mesh B.S. sieve and thoroughly mixed with a known proportion by weight of finely divided zinc oxide. The X-ray diffraction pattern was recorded using nickel-filtered copper radiation. McCreery's<sup>1</sup> specimen holders are recommended when a diffractometer is employed to obtain diffraction patterns. Under these conditions only that part of the pattern from  $12^\circ$  to  $20^\circ$  is required. We have obtained good results scanning at a speed of  $1^\circ$  per minute, and averaging the results from two scans in each direction. Taking the height of the  $3.195\text{\AA}$  arsenious oxide peak above the background as representing an intensity of 100 units, the intensities of the  $2.768\text{\AA}$  and  $2.541\text{\AA}$  peaks from arsenious oxide and the zinc oxide peaks at  $2.816\text{\AA}$ ,  $2.602\text{\AA}$  and  $2.476\text{\AA}$  were measured. The diffraction patterns were normalised and the concentration of arsenious oxide calculated by Brentano's<sup>2</sup> procedure.

## RESULTS

A knowledge of the intensity of the diffraction peaks from the pure compounds is required for the application of Brentano's method of analysis. This method gives more reliable results than analyses based on one line each from the unknown and the internal standard. Calculations from 12 or more independent measurements of intensity ratios for the pure compounds gave an average coefficient of variation of 8. This figure was considered to be satisfactory since the X-ray tube output was not stabilised or monitored. Table 1 compares our results with data obtained by Swanson and Tatge<sup>3</sup> and by Swanson and Fuyat<sup>4</sup>.

TABLE I  
*Relative intensity measurements for arsenious oxide and zinc oxide*

Spacing (Å)	Present Work As <sub>2</sub> O <sub>3</sub>	ZnO	Swanson <i>et al.</i> <sup>3,4</sup> As <sub>2</sub> O <sub>3</sub>	ZnO
3.195	100		100	
2.768	31		28	
2.541	41		38	
2.816		64		71
2.602		48		56
2.476		100		100

Fig. 1 shows the calibration curve obtained with known mixtures of pure arsenious oxide and zinc oxide. The points fall close to a smooth curve.

The mixtures of sulphur and arsenic compounds investigated were shown to contain, in addition to arsenious oxide, an unidentified compound which liberated arsenious oxide when dissolved in water. Wet chemical methods of analysis were therefore not applicable.

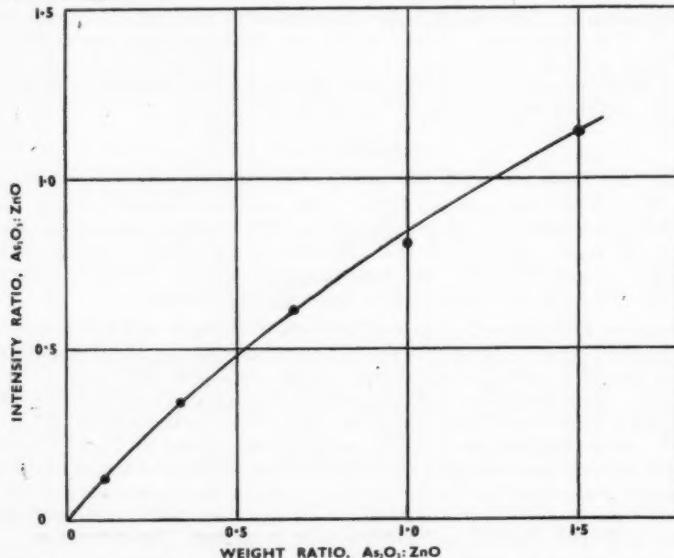


Fig. 1—X-ray intensity ratios for arsenious oxide—zinc oxide mixtures

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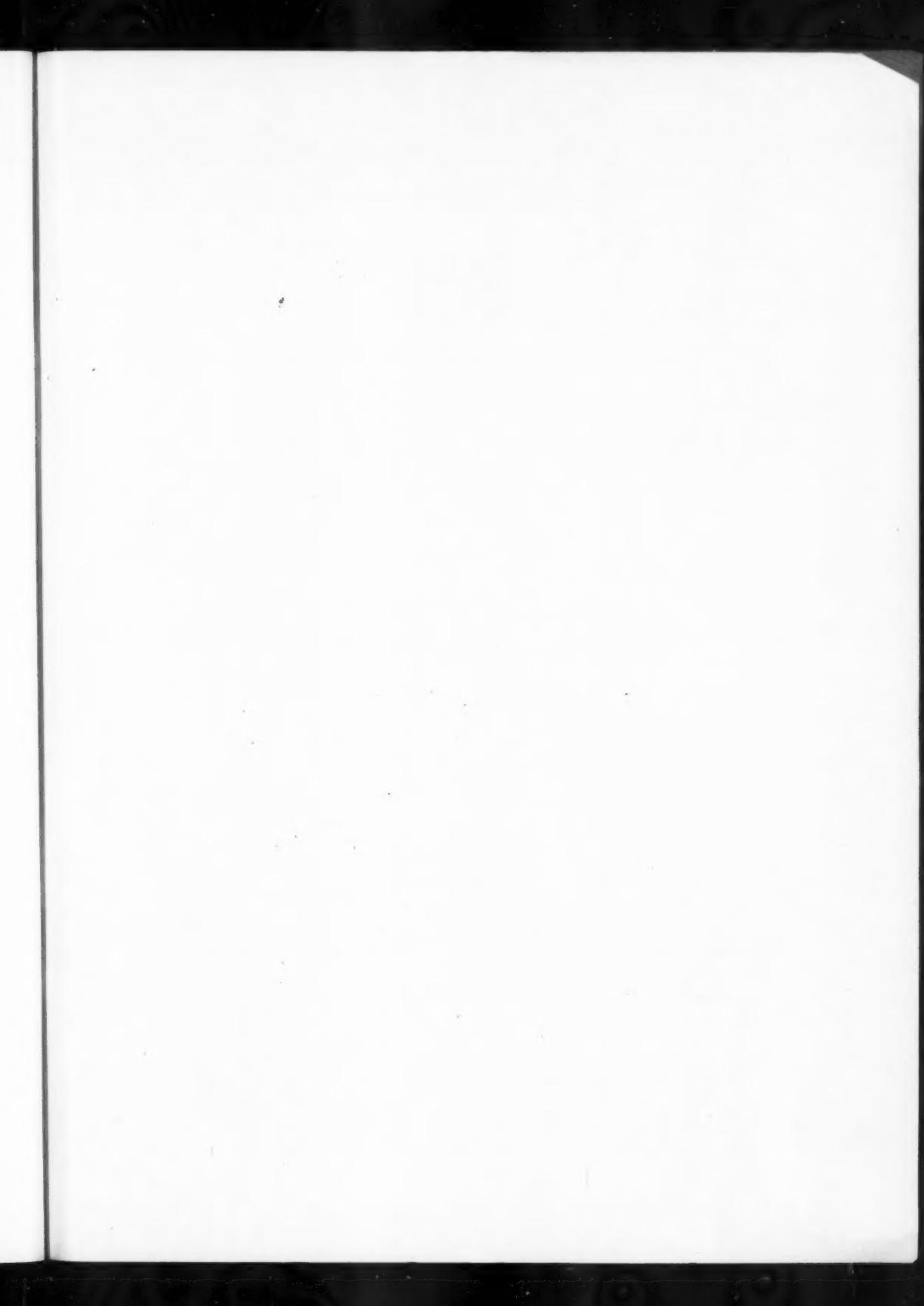
Research Department,  
African Explosives and Chemical Industries, Limited,  
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Transvaal.

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REFERENCES

- <sup>1</sup> McCreery, *J. Amer. Ceram. Soc.*, 1949, **32**, 141.
- <sup>2</sup> Brentano, *J. Appl. Phys.*, 1949, **20**, 1215.
- <sup>3</sup> Swanson and Tatge, *J.C. Fel. Reports N.B.S.*, 1949.
- <sup>4</sup> Swanson and Fuyat, *N.B.S. Circular No. 539*, Vol. II, 1953.







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